STATISTICAL THERMODYNAMICS

OF

CRYSTAL LATTICES

Thesis

for the Degree of Doctor of Philosophy

submitted by

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INTRODUCTION.

This work is the development of a new approach to the theory of thermodynamical equilibrium in the ideal solid state, recently put forward by Professor Max Born (1951a, 1951b). His purpose was to overcome a fundamental expansion difficulty in the usual theory and to generalise it to include strongly anharmonic effects (such as exist in solid helium); it was also hoped to provide alternative solutions of the non-linear vibrational equations which might indicate intrinsic imperfections ("block-structure" -- see Born (1947), Fürth (1949)) in the equilibrium state. Such solutions have not been found; even in the non-linear case an ideal lattice configuration can be proposed as a solution (though perhaps not the only one), with some changes as discussed by Born (1951a), and the atoms can be taken to vibrate about this reference configuration with stable, fourth degree oscillations. By a method of adaptation independent harmonic modes of vibration can be chosen to be a close approximation to the atomic motion, whatever the reference configuration, and the corresponding thermodynamical formulae may be developed either for large anharmonic

effects or by treating the third and fourth degree terms in the potential energy as a small perturbation.

Instead of at the start taking the atoms to vibrate about the minimum-energy configuration, which leads to the fundamental difficulty that their mean displacements increasingly diverge from these positions as the size of the specimen increases, owing to the anharmonicity, we keep the reference configuration free and fix its coordinates as the quantum mechanical average positions at a later stage of the calculation; in this way both zero-energy and temperature effects can be properly accounted for and the vibrations can always be regarded as (relatively) small compared to the atomic spacing. At the same time, new effective harmonic lattice frequencies are established which reduce in a continuous fashion to those of the ordinary quadratic theory when the vibrations are very small.

In his second paper (1951b) Born has established the use of a potential function having the nuclear coordinates (χ) alone as variables without the prior fixing of their reference positions as in the previous method (Born & Oppenheimer, 1927).

For an insulator, which is all that we shall consider, only the ground state of the electronic motion is important, and this provides an energy operator $\mathcal{U}(x)$, say, such that the Hamiltonian $\mathcal{H}$ of the atomic system is

$$\mathcal{H} = \frac{1}{2}\sum_{\ell} \frac{p_\ell^2}{m_\ell} + \mathcal{U}(x),$$

satisfying the Schrödinger equation

$$(\mathcal{H} - \mathcal{E}_n)\,\Psi_n(x) = 0.$$

It is convenient to deal with the vibrational energy alone, $\mathcal{H} - \mathcal{U}_0$, $\mathcal{E}_n - \mathcal{U}_0$, $\mathcal{U}(x) - \mathcal{U}_0$, so that the potential energy can be expanded in powers of (x), starting with the <u>first</u>, where $\mathcal{U}_0$ is the static potential energy in the reference configuration. We shall use the symbols $\mathcal{H}$, $\mathcal{E}_n$, $\mathcal{U}(x)$, to refer to these <u>vibrational</u> quantities in general, the meaning being clear from the context. Script letters ($\mathcal{H}$, $\mathcal{E}$, etc.) will be restricted to the actual atomic system, and block letters (H, E, etc.) will be used for the adapted harmonic approximation mentioned above.

The general theory will first be developed, then the theoretical example of a monatomic linear

chain will be worked out in full, both to illustrate the three dimensional theory and to provide approximations for later work, and finally an application of the non-linear results to the thermal behaviour of solid helium will be made.

I wish to express my sincere thanks to Professor Max Born for introducing me to this subject and for much helpful advice and encouragement during its development.

CHAPTER 1: QUANTUM THEORY OF THE IDEAL SOLID STATE.

1a: The Adaptation Method.

We may write the vibrational potential energy ($\mathcal{U}$) of a system of atoms in thermal equilibrium in the solid state as

$$\mathcal{U} = \mathcal{U}_1 + \mathcal{U}_2 + \mathcal{U}_3 + \mathcal{U}_4 + \cdots , \tag{1.1}$$

where

$$\left.\begin{aligned} \mathcal{U}_1 &= \sum_{\ell} \mathcal{U}_{\ell} (x_{\ell} - x_{\ell}^{ref}) \\ \mathcal{U}_2 &= \tfrac{1}{2!} \sum_{\ell\ell'} \mathcal{U}_{\ell\ell'} (x_{\ell} - x_{\ell}^{ref})(x_{\ell'} - x_{\ell'}^{ref}) \\ &\cdots\cdots\cdots \end{aligned}\right\} , \tag{1.2}$$

the various coordinates x_{ℓ} being such that each can be related to some one reference position x_{ℓ}^{ref} so that the relative displacements $x_{\ell} - x_{\ell}^{ref}$ are small. If the system comprises N atoms in a three dimensional solid the $\ell, \ell', \ldots$ will have the values $1, 2, \ldots 3N$. The $\mathcal{U}_{\ell}, \mathcal{U}_{\ell\ell'}, \ldots$ stand for the derivatives of $\mathcal{U}$ with respect to the corresponding x_{ℓ} , taken in the reference configuration x_{ℓ}^{ref} .

For the present we will consider all terms $\mathcal{U}_r$

up to the fourth degree as of equal importance, and neglect the rest by comparison: the vibrational motion in the solid is thus to be regarded as essentially anharmonic, and our purpose is to put forward an harmonic approximation to it. The case when the terms of third and fourth degree in the displacements are themselves small in comparison to the linear and quadratic is automatically covered if we later replace "non-linear" solutions by "perturbation" solutions.

By analogy with the usual procedure of choosing normal coordinates we consider a real+ linear canonical transformation, of orthogonal matrix $[e_{\ell m}]$, applied to the coordinates x_ℓ and momenta p_ℓ such that

$$x_\ell - x_\ell^{eq} = \frac{1}{\sqrt{m_\ell}} \sum_m e_{\ell m} q_m ,$$

$$p_\ell = \sqrt{m_\ell} \sum_m e_{\ell m} p_m , \qquad (1.3)$$

where p_m is the momentum conjugate to the new coordinate q_m, and $m = 1 \ldots 3N$. The orthogonality of $[e_{\ell m}]$ implies

+ The theory could be stated in complex terms, but this is of no advantage here.

$$\left.\begin{aligned} \sum_{\ell} e_{\ell n} e_{\ell n'} - \delta_{nn'} &= 0 \\ \sum_{n} e_{\ell n} e_{\ell' n} - \delta_{\ell\ell'} &= 0 \end{aligned}\right\} . \qquad (1.4)$$

The potential energy $u(x)$ goes over into $v(q)$ where

$$v = v_1 + v_2 + v_3 + v_4 + \cdots ,$$

$$v_1 = \sum_{n} v_n q_n , \qquad v_n = \sum_{\ell} \frac{e_{\ell n}}{\sqrt{m_\ell}} u_\ell ,$$

$$v_2 = \frac{1}{2!} \sum_{nn'} v_{nn'} q_n q_{n'} , \quad v_{nn'} = \sum_{\ell\ell'} \frac{e_{\ell n} e_{\ell' n'}}{\sqrt{m_\ell m_{\ell'}}} u_{\ell\ell'} , \qquad (1.5)$$

$$\cdots \cdots \cdots \cdots$$

while the kinetic energy transforms according to

$$\frac{1}{2} \sum_{\ell} \frac{p_\ell^2}{m_\ell} = \frac{1}{2} \sum_{n} p_n^2 . \qquad (1.6)$$

In the usual theory the linear terms v_1 are made to vanish, the x_ℓ^{ref} being chosen so that $u_\ell = 0$, $\ell = 1, \ldots 3N$, and no higher than quadratic terms in u or v are considered. The $e_{\ell n}$ are taken as those $e^0_{\ell n}$ which make these quadratic terms diagonal,

$$\sum_{\ell\ell'} \frac{e^0_{\ell n} e^0_{\ell' n'}}{\sqrt{m_\ell m_{\ell'}}} u_{\ell\ell'} = \delta_{nn'} \omega_n^{0\,2} , \text{ say,} \qquad (1.7)$$

and for ordinary solids the $\omega_n^{0\,2}$ so defined are

positive. The Hamiltonian of the system can then be written

$$H^0 = \tfrac{1}{2}\sum_\nu p_\nu^2 + \tfrac{1}{2}\sum_\nu \omega_\nu^{0\,2} q_\nu^2 \qquad (1.8)$$

which is just that of a set of $3N$ independent harmonic oscillators; these constitute the normal modes of vibration of the system.

In the presence of third and fourth degree terms, even if the $e_{\ell\nu}$ were still chosen according to (1.7) -- as in fact they will be at a later stage in our solution -- (1.8) would not represent the whole vibrational energy of the system; this would be

$$H^0 + V_3^0 + V_4^0 + \cdots, \qquad (1.9)$$

the ^{0} denoting the appearance of the known $e_{\ell\nu}^0$, ω_ν^0, and if the choice of reference positions $u_\ell = 0$ were dropped, it would be

$$\mathcal{H}^0 = H^0 + V_1^0 + V_3^0 + V_4^0 + \cdots. \qquad (1.9')$$

It might also happen that the $\omega_\nu^{0\,2}$ were no longer positive so that (1.8) could not represent a system of harmonic oscillators at all: this is the state of affairs in solid helium at molar volumes of ~14cc

or more; the third and fourth degree terms, rather than the second, then control the vibrations of the atoms.

The Hamiltonian in the anharmonic case can be written quite generally according to (1.5), (1.6) as

$$\mathcal{H} = \tfrac{1}{2}\sum_n p_n^2 + V_1 + V_2 + V_3 + V_4 + \cdots . \qquad (1.10)$$

Instead of comparing (1.9) with (1.8), and treating the anharmonic terms ($V_1^0 = 0$) as a perturbation of H^0 -- the usual procedure for extending the quadratic theory -- we will compare the general Hamiltonian (1.10) with that of an arbitrary system of independent harmonic oscillators having (real) frequencies ω_n :

$$H = \tfrac{1}{2}\sum_n p_n^2 + \tfrac{1}{2}\sum_n \omega_n^2 q_n^2 . \qquad (1.11)$$

It will be our object to adapt these oscillators to the system in such a way that they will represent the actual motion as closely as possible over a range of temperatures and in those circumstances quoted above in which the method based on (1.8) fails. It will be found that the difference in energies

$$W \equiv \mathcal{H} - H = V_1 + \tilde{V}_2 + V_3 + V_4 + \cdots , \qquad (1.12)$$

where

$$\tilde{V}_2 = \frac{1}{2!}\sum_{nn'} \tilde{V}_{nn'} q_n q_{n'}\,, \qquad \tilde{V}_{nn'} = V_{nn'} - \delta_{nn'}\omega_n^2\,, \tag{1.13}$$

can be treated as a perturbation of H and that just sufficient equations can be provided to determine the quantities x_ℓ^{nq}, $e_{\ell n}$, ω_n which appear as parameters in (1.3) - (1.13). The choice of $e_{\ell n}$ as $e_{\ell n}^0$ would imply that W takes the form

$$\begin{aligned} W^0 &= \mathcal{H}^0 - H \\ &= (H^0 - H) + V_1^0 + V_3^0 + V_4^0 + \cdots, \end{aligned} \tag{1.14}$$

and the frequencies ω_n would remain to be determined as distinct from the (possibly imaginary) ω_n^0.

The "normal modes of vibration" of the system, in the coordinates q_n, are no longer harmonic, nor are they independent, as the Hamiltonian (1.10) shows; we may, however, regard them approximately as the independent harmonic oscillations defined by (1.11); if the choice $e_{\ell n}^0$ is made they have, approximately, all the properties of the usual normal modes except that their frequencies are new, determined by the anharmonic terms

in the potential, and this will be found to provide a useful approach over the whole range of data available for solid helium.

1b: The Partition Function.

The thermodynamical properties are determined by the free energy

$$\mathcal{F} = u_0 - \frac{1}{\beta} \log \zeta \,, \tag{1.15}$$

u_0 being the static potential energy, and ζ the partition function

$$\zeta = \sum_n e^{-\varepsilon_n \beta} \,, \tag{1.16}$$

the ε_n being the energy levels of the Hamiltonian $\mathcal{H}$ given by (1.10); β is $\frac{1}{kT}$.

We will suppose that these ε_n can be derived from the energy levels E_n of the system of oscillators (1.11) by the application of the perturbation W of (1.12), so that we may write

$$\varepsilon_n = E_n + \Delta_n \,,$$

Δ_n being the change in the n^{th} energy level

of the oscillator system[+], to be obtained formally by the usual perturbation equations -- this is considered in chapter 2. We may note here that $\mathcal{E}_n$, E_n , Δ_n are all proportional to N , the size of the system; for one mole of solid helium they are $\sim 10^9$ ergs, the order of magnitude of the zero energy $\mathcal{E}_0$. The average thermal excitation at low temperatures ($T \sim 10^\circ K$; $\beta \simeq 1 \times 10^{15}$ ergs^{-1}) is $\sim 10^8$ ergs/mole.

If the partition function of the oscillator system is written

$$\mathcal{Z} = \sum_n e^{-E_n \beta} , \tag{1.17}$$

we have from (1.15)

$$\mathcal{Z} = \sum_n e^{-\mathcal{E}_n \beta} e^{-\Delta_n \beta}$$

$$= \mathcal{Z} \overline{e^{-\Delta_n \beta}} ,$$

(1.18)

+ The quantum number n is really $(n) = (n_1, n_2 \cdots n_{3N})$ and

$$E_n = (E_1)_{n_1} + (E_2)_{n_2} + \cdots + (E_{3N})_{n_{3N}}$$

$$= (n_1 + \tfrac{1}{2})\hbar\omega_1 + \cdots + (n_{3N} + \tfrac{1}{2})\hbar\omega_{3N} ;$$

it should be noted that $\Delta_n = \Delta_{(n_1, n_2, \ldots n_{3N})}$ is <u>not</u> of the form $(n_1 + \tfrac{1}{2})\hbar\omega_1 + \cdots$, since the frequencies are unchanged: the perturbation Δ_n can only in part be split up into a sum of terms, one for each oscillator and depending on the number n_k .

the bar denoting a Boltzmann average over the oscillator system at temperature T : for any operator A ,

$$\overline{A} = \frac{\sum_n e^{-E_n\beta} A_{nn}}{\sum_n e^{-E_n\beta}} = \frac{\sum_n e^{-E_n\beta} A_{nn}}{Z} . \qquad (1.19)$$

We can write

$$\Delta_n = \Delta_0 + \Delta_n^T ,$$

Δ_0 being the perturbation of the ground state and Δ_n^T that of the thermal excitation in the state n . The exponential in (1.18) is then $e^{-\Delta_0\beta} \cdot e^{-\Delta_n^T\beta}$, where $\Delta_n^T\beta \sim 10^8 \cdot 10^{15} = 10^{23}$; this should really be regarded as $\left(e^{-\delta_0\beta} \cdot e^{-\delta_n^T\beta}\right)^N$, since the logarithm of this quantity -- which appears in the free energy -- must be proportional to N : here $\Delta_n = N\delta_n$, δ_n being proportional to the energy of a single oscillator, $\sim 10^{-15}$ erg, and (1.18) is to be written

$$\zeta = Z e^{-\Delta_0\beta} \overline{\left(e^{-\delta_n^T\beta}\right)^N} ; \qquad (1.18')$$

the problem is to evaluate this average of the N^{th} power of the exponential. The argument $\delta_m^T \beta \sim 1$ so that a direct expansion of $e^{-\delta_m^T \beta}$ will not converge well -- this is the real limitation of the method, imposed by the very low helium temperatures at which we wish to work.

Using the formal quantity $e^{-\Delta_m \beta}$ for the present, we may also consider (1.18) as

$$\zeta = \sum e^{-\overline{\Delta_m}\beta} \overline{e^{-(\Delta_m^T - \overline{\Delta_m^T})\beta}} , \qquad (1.18'')$$

where $\overline{\Delta_m}$ is the thermal (oscillator) average of the changes in the energy levels, and $\overline{\Delta_m^T}$ the average change in their excitation. It is clear that

$$\overline{e^{-(\Delta_m^T - \overline{\Delta_m^T})\beta}} = 1 + \frac{1}{2!}\beta^2 \overline{(\Delta_m^T - \overline{\Delta_m^T})^2} - \frac{1}{3!}\beta^3 \overline{(\Delta_m^T - \overline{\Delta_m^T})^3} + \cdots$$

$$\sim \left[1 + \frac{a_2}{2!}\beta^2 N \overline{(\delta_m^T - \overline{\delta_m^T})^2} - \frac{a_3}{3!}\beta^3 N^2 \overline{(\delta_m^T - \overline{\delta_m^T})^3} + \cdots \right]^N , \qquad (1.20)$$

since $\Delta_m^2 = N^2 \delta_m^2$, ---- , the a_r being some constants ~ 1 ; we may expect the mean-square deviation $\overline{(\Delta_m^I - \overline{\Delta_m^I})^2}$ of the system of $3N$ oscillators to be proportional to N , as it relates to a kind of multinomial statistical distribution, and so $N\overline{(\delta_m^I - \overline{\delta_m^I})^2}$ to be proportional to the squared thermal energy of a single oscillator -- $\beta^2 N \overline{(\delta_m^I - \overline{\delta_m^I})^2}$ is then ~ 1 in agreement with the remarks above.

As a first approximation by which to proceed, we will neglect all but the first term of (1.20), which is the same as replacing $\overline{e^{-\Delta_m \beta}}$ by $e^{-\overline{\Delta}_m \beta}$ in (1.18); a strict consideration of the effect of the expansion (1.20) will not be carried out here: the present approximation can be made to give very good results in the helium application.

Using (1.18) we may then write the free energy (1.15) as

$$\mathcal{F} = u_0 - \frac{1}{\beta} \log Z + \overline{\Delta_m}, \tag{1.21}$$

and it remains to determine the average energy perturbation $\overline{\Delta_m}$ as a function of the "adapted" parameters x_ℓ^{ad}, e_m , ω_r : this is done to

a sufficient approximation in the next chapter. The first two terms of (1.21) are of the usual harmonic form, with

$$Z = \prod_{k}^{(3N)} 2\sinh\left(\tfrac{1}{2}\hbar\omega_k\beta\right); \qquad (1.22)$$

in the ordinary theory ω_k^0 appears instead of ω_k. The additional term $\overline{\Delta_n}$ depends primarily on the quadratic and fourth degree perturbation terms, $\tilde{V}_2$ and V_4 : $\tilde{V}_2$ of course vanishes if the ordinary choice of oscillators, $H = H^0$, is made.

1c: The Density Matrix.

The original method of applying this adaptation procedure (see Born (1951a)) made use of the density matrix of quantum mechanics, the purpose being to avoid the complexity of a full solution of Schrödinger's equation and subsequent averaging by Boltzmann factors. Thermal averages, and non-equilibrium phenomena, are also more readily tackled through the density matrix. In coordinate representation the density matrix is

$$\rho(q,q'|\beta) = \sum_n \Psi_n^*(q')\, e^{-\beta E_n}\, \Psi_n(q), \qquad (1.23)$$

Ψ_n being the eigenfunction belonging to $\mathcal{E}_n$; it satisfies Bloch's equation

$$\frac{\partial \rho}{\partial \beta} = -\frac{1}{2}\left(\mathcal{H}\rho + \rho\mathcal{H}\right) \tag{1.24}$$

and is connected with the partition function by the formula

$$Z = \int \rho(q,q|\beta)\,dq\,; \tag{1.25}$$

the thermal average of any operator A is given by

$$\langle A \rangle = \frac{\int A(q,q)\,\rho(q,q|\beta)\,dq}{\int \rho(q,q|\beta)\,dq}\,. \tag{1.26}$$

It was proposed to write

$$\left.\begin{aligned} \rho &= \sigma q \\ q &= 1 + q_1 + q_2 + \cdots \end{aligned}\right\}, \tag{1.27}$$

where $\sigma(q,q'|\beta)$ is the density matrix of the oscillators $\mathcal{H}$, and q_n a polynomial of degree n in the coordinates q , q' . It then follows that

$$\chi = \int \sigma q \, dq$$

$$= \chi \bar{q} \,, \tag{1.28}$$

where for any operator the average over the oscillators is

$$\overline{A} = \frac{\int A(q,q) \, \sigma(q,q|\beta) \, dq}{\int \sigma(q,q|\beta) \, dq} \,. \tag{1.29}$$

From the Bloch equation (1.24) an equation in q could then be derived, dependent on the known form of σ (Husimi, (1940)); this was to be solved by successive polynomial approximations.

The relation between this method and that of section 1b is immediately obvious: from (1.18), (1.28), it follows that

$$\bar{q} = \overline{e^{-\Delta_n \beta}} = e^{-\bar{\sigma}_n \beta} \, \overline{e^{-(\sigma_n - \bar{\sigma}_n)\beta}} \,, \tag{1.30}$$

and the formal expansions

$$\overline{q} = 1 + \overline{q}_1 + \overline{q}_2 + \cdots,$$

$$\overline{e^{-\sigma_w \beta}} = \left(1 - \beta\overline{\sigma}_w + \cdots\right)\left(1 + \frac{1}{2!}\beta^2\overline{(\sigma_w^I - \overline{\sigma_w^I})^2} - \cdots\right) \tag{1.31}$$

must be equivalent.

It was found possible to develop a symmetrical method of solving the equations for the q_w in (1.27), dependent on simple integrations; the approximations used correspond exactly to the omission of terms that will be made in chapter 2. The averaged results, arranged according to products of the $\overline{q}_w^2$ +, were just the terms of $\beta\overline{\sigma}_w$; no higher powers of β appear in the first few polynomials considered. But these $\overline{q}_w$ involved terms of a large order of magnitude ($\sim N$) and to put the method on a proper footing we should write

$$\left.\begin{aligned} \rho &= \sigma q^N \\ q &= 1 + q_1 + q_2 + \cdots \end{aligned}\right\},$$

+ This polynomial method corresponds really to the "perturbation" case considered below in which third and fourth degree terms in V are to be considered small compared with the harmonic part.

which would give rise to new equations for the q_m. Instead of (1.31) there would be a development

$$\overline{q^N} \sim \left[1 + \overline{q_1'} + \overline{q_2'} + \cdots \right]^N$$

to correspond with (1.20):

$$\overline{\left(e^{-\delta_m \beta}\right)^N} \sim \left[\left(1 - \beta \delta_m + \cdots\right)\left(1 + \frac{1}{2!} a_2 \beta^2 N \overline{(\delta_m^I - \delta_m^{\bar{I}})^2} + \cdots\right) \right]^N .$$

The higher polynomials could then be properly discounted, apart from bad convergence due to the large value of β.

For these reasons the formal development of the $\mathcal{J}$-theory mentioned above will not be included here; however, the solution to the average conditions originally proposed for adapting the oscillators H to the system H which it provided will be quoted in chapter 2.

CHAPTER 2: THE ADAPTATION CONDITIONS.

2a: Their Derivation.

To determine the partition function and free energy of the atomic system we need to know the $\overline{\Delta_n}$ of the previous chapter corresponding to the perturbing energy (1.12):

$$W = \sum_n V_n q_n + \frac{1}{2!}\sum_{nn'} \tilde{V}_{nn'} q_n q_{n'} + \cdots . \tag{2.1}$$

The usual perturbation formulae may be applied to give, as the first, second, ... order changes

$$\Delta_n^{(1)} \ , \ \Delta_n^{(2)} \ , \ \cdots\cdots \ ,$$

$$\Delta_n^{(1)} = W_{nn}, \ ^{+}$$

$$\Delta_n^{(2)} = \sum_n{}' \frac{|W_{nn}|^2}{E_n - E_n} \ , \tag{2.2}$$

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and the thermal averages $\overline{\Delta_n^{(1)}}$, $\overline{\Delta_n^{(2)}}$, ... are required.

+ These are the matrix elements in the energy representation of the oscillator system

$$W_{nn} = \int \psi_n^*(q)\, W(q,q)\, \psi_n(q)\, dq),$$

$\psi_n(q)$ being the oscillator eigenfunction belonging to E_n , and (q) meaning the set of $3N$ variables q_k .

In the limit as $T \to 0$ $\bar{\Delta}_n$ goes over into Δ_0, the perturbation of the zero energy, and at the low helium temperatures to be considered the two are not very different. We shall consider Δ_0 in full to the second order, and from the limiting form of the result infer what $\bar{\Delta}_n$ is expected to be, at low T, except perhaps for small corrections.

The first order perturbation $\overline{\Delta_n^{(1)}}$ can immediately be written down in full: from the definition of the oscillator average expressed by (1.19), and the form of (2.1), we have

$$\overline{\Delta_n^{(1)}} = \frac{1}{Z}\sum_n e^{-E_n\beta}\left\{\frac{1}{2!}\sum_n \tilde{v}_{nn}(q_n^2)_{nn} + \frac{3}{4!}\sum_{nn'} V_{nnn'n'}(q_n^2)_{nn}(q_{n'}^2)_{nn} + \cdots\right\}$$

$$= \frac{1}{2}\sum_n \tilde{v}_{nn}\bar{q}_n^2 + \frac{1}{4.2!}\sum_{nn'} V_{nnn'n'}\bar{q}_n^2\bar{q}_{n'}^2 + \cdots, \qquad (2.3)$$

all other terms vanishing since we are dealing with independent harmonic oscillators.

In the case of a lattice many of the oscillators will be expected to have the same frequency, the energy levels E_n being correspondingly

degenerate; in any case, these levels will lie very close, $\sim 10^{-16}$ erg apart (due to single oscillators) compared to their absolute magnitude $\sim 10^{9}$ erg. However, this spacing may still be considered discrete in regard to the higher order terms of the perturbation since, from the form of (2.1), the matrix elements of W for closely neighbouring states also depend only on single oscillators and are correspondingly small. In the first order there is no difficulty; neither does the degeneracy matter, since we are concerned with the average $\overline{\Delta_m^{(1)}}$ alone: the same Boltzmann factor $e^{-E_m\beta}$ applies to the various $\Delta^{(1)}_{m m_s}$ which arise from a degenerate E_m, so that we need their arithmetic mean only; this is proportional to the trace $\sum_s W_{m_s m_s}$ of the m^{th} submatrix of $[W_{mn}]$ belonging to the states of energy E_m, and may be included with all other diagonal elements W_{mm} in the same expression $\sum_m e^{-E_m\beta} W_{mm} / z$ for $\overline{\Delta_m^{(1)}}$.

Similar considerations must apply to the higher order perturbations if any degeneracy remains: we shall here consider only the nondegenerate ground state E_0 in any detail.

Because of the polynomial form (2.1) of W

the matrix elements $W_{mm'}$ defined in the footnote to (2.2) can all be expressed as the sum of terms like

$$\prod_{n}^{(3N)} \left\{ \int \psi^{*}_{m_n}(q_n)\, \psi_{m'_n}(q_n)\, q_n^{\tau_n}\, dq_n \right\} = \prod_{n}^{(3N)} \left(q_n^{\tau_n}\right)_{m_n m'_n}, \qquad \tau_n = 0,1,2,\ldots, \tag{2.4}$$

since $\psi_m(q) = \psi_{m_1}(q_1)\psi_{m_2}(q_2)\cdots\psi_{m_{3N}}(q_{3N})$, the oscillators being independent. Further,

$$\psi_{m_n}(q_n) = H_{m_n}(a_n)\, e^{-\frac{1}{4} q_n^2/a_n^2}, \tag{2.5}$$

where H_{m_n} is the Hermite polynomial of degree m_n, and a_n is given by +

$$a_n^2 = \frac{1}{2}\frac{\hbar}{\omega_n} = \lim_{T\to 0} \overline{q_n^2}. \tag{2.6}$$

In the linear terms of W, τ_n can be 0 or 1, in the quadratic terms, 0, 1, or 2, and so on; it is well known that when τ_n is even, $|m_n - m'_n|$ must be even, and when τ_n is odd, $|m_n - m'_n|$ must be odd -- otherwise the matrix element $\left(q_n^{\tau_n}\right)_{m_n m'_n}$ vanishes; further, $\left(q_n^{\tau_n}\right)_{m_n m'_n}$ is zero whenever $|m_n - m'_n| > \tau_n$.

+ In this work the zero frequencies (translations) must be avoided by putting the corresponding displacements arbitrarily to zero: the effect is to omit the corresponding indices in any sums $\sum_n$.

The transitions $(n) \to (m)$ which have non-vanishing matrix elements W_{nm} are thus severely restricted, and the various W_{nm} can be written down without much trouble.

From the ground state $(n) = (0)$ the k^{th} linear term of W appears only for $(m) = (0,0,\dots m_k=1, 0,\dots 0) = (01)_k(00)$, say; all other terms of W which are odd in q_k also contribute to this matrix element $W_{(01)_k(00)}$. To the terms of third degree, it follows at once from the known matrix elements of the powers of q_k that

$$W_{(01)_k(00)} = a_k \left\{ V_k + \frac{1}{2!} \sum_{k'} V_{kkk'} a_{k'}^2 \right\},$$

and since the energy difference is

$$E_{(0)} - E_{(01)_k(00)} = -\hbar\omega_k$$

the corresponding term of the second order perturbation $\Delta_0^{(2)}$ (by (2.2)) is

$$\frac{W_{(01)_k(00)}^2}{E_{(0)} - E_{(01)_k(00)}} = -\frac{1}{\hbar} \frac{a_k^2}{\omega_k} \left\{ V_k + \frac{1}{2!} \sum_{k'} V_{kkk'} a_{k'}^2 \right\}^2;$$

the contribution of all the linear terms of W is contained in

$$-\frac{1}{\hbar}\sum_{k}\frac{a_k^2}{\omega_k}\left\{V_k+\frac{1}{2}\sum_{k'}V_{kk'k'}\,a_{k'}^2\right\}^2 . \qquad (2.7)$$

The cubic terms also appear in the matrix elements $W_{(03)_k(00)}$, $W_{(02)_k(01)_{k'}(00)}$, $W_{(01)_k(01)_{k'}(01)_{k''}(00)}$, with an obvious notation; it is readily shown that these give the contribution to $\Delta_0^{(2)}$

$$-\frac{1}{\hbar}\frac{1}{3!}\sum_{kk'k''}\frac{a_k^2 a_{k'}^2 a_{k''}^2}{\omega_k+\omega_{k'}+\omega_{k''}}\,V_{kk'k''}^2 . \qquad (2.8)$$

For the quadratic terms the matrix elements $W_{(02)_k(00)}$, $W_{(01)_k(01)_{k'}(00)}$ must be considered, and these affect all other even terms as well. To the fourth degree we find, in exact analogy to (2.7) and (2.8), that the whole contribution of the quadratic terms is contained in

$$-\frac{1}{\hbar}\frac{1}{2!}\sum_{kk'}\frac{a_k^2 a_{k'}^2}{\omega_k+\omega_{k'}}\left\{\tilde{V}_{kk'}+\frac{1}{2}\sum_{k''}V_{kk'k''k''}\,a_{k''}^2\right\}^2 , \qquad (2.9)$$

and the remaining contribution of the quartic terms in

$$-\frac{1}{k}\frac{1}{4!}\sum_{kk'k''k'''}\frac{a_k^2 a_{k'}^2 a_{k''}^2 a_{k'''}^2}{\omega_k+\omega_{k'}+\omega_{k''}+\omega_{k'''}}\,V^2_{kk'k''k'''}\,.$$

(2.10)

Now, with a_k^2 given by (2.6) and $\sim \overline{q_k^2} = \frac{E_k}{\omega_k^2}$ at low T (E_k is the vibrational energy of a quantum oscillator of frequency ω_k), and since in the helium case the average effect of quadratic and fourth degree terms is assumed to be comparable, $\tilde{V}_{kk'} \sim \frac{1}{2}\sum_{k''} V_{kk'k''k''}\overline{q_{k''}^2} \sim \omega^2$, we can estimate that (2.9), (2.10) are proportional to the total oscillator energy $(\sim N)$ -- as we should expect -- and that (2.10) is considerably the smaller in magnitude. Similar results would apply to (2.7), (2.8). We shall in what follows neglect the two terms (2.10), (2.8) by comparison with those containing the curly brackets, (2.9), (2.7). Again, remembering the limiting form of a_k^2 given above, and by comparison with the form of $\overline{\Delta_\omega^{(1)}}$, we will infer that $\overline{\Delta_\omega^{(2)}}$ is to be derived from $\Delta_0^{(2)}$ by replacing $a_k^2 = \lim_{T\to 0}\overline{q_k^2}$ by $\overline{q_k^2}$ itself: any small corrections will be neglected along with (2.10), (2.8). Thus we

may write, to the second order in the perturbation W,

$$\overline{\Delta_n} = \sum_n \left(\tfrac{1}{2}\bar{q}_n^2\right)\tilde{V}_{nn} + \tfrac{1}{2}\sum_{nn'}\left(\tfrac{1}{2}\bar{q}_n^2\right)\left(\tfrac{1}{2}\bar{q}_{n'}^2\right)V_{nnn'n'}$$

$$- \sum_n \frac{\left(\tfrac{1}{2}\bar{q}_n^2\right)}{E_{0n}}\left\{V_n + \sum_{n'}\left(\tfrac{1}{2}\bar{q}_{n'}^2\right)V_{nn'n'}\right\}^2$$

$$- \frac{1}{2!}\sum_{nn'}\frac{\left(\tfrac{1}{2}\bar{q}_n^2\right)\left(\tfrac{1}{2}\bar{q}_{n'}^2\right)}{\tfrac{1}{2}(E_{0n}+E_{0n'})}\left\{\tilde{V}_{nn'} + \sum_{n''}\left(\tfrac{1}{2}\bar{q}_{n''}^2\right)V_{nn'n''n''}\right\}^2$$

$$+ \cdots\cdots ; \qquad (2.11)$$

the symmetry of this result suggests that higher orders in the perturbation could be written down fairly simply: we will not go any further here.

As mentioned in 1c, the formal expansion of the density matrix method has given rise to just the terms appearing in (2.11), though differently arranged, and this suggests strongly that the inference from $\Delta_0^{(2)}$ to the general form of (2.11) is correct. The adaptation of the oscillators in that method was made by applying average conditions of the kind

$$\langle A \rangle = \overline{A}$$

(with $\langle A \rangle$ defined by (1.26) and $\overline{A}$ by (1.19) or (1.29)) to the coordinates q_n and pairs of coordinates $q_n q_{n'}$,

$$\left.\begin{aligned} \langle q_n \rangle &= \overline{q_n} = 0 \\ \langle q_n q_{n'} \rangle &= \overline{q_n q_{n'}} = \delta_{nn'} \overline{q_n^2} \end{aligned}\right\}, \qquad (2.12)$$

and it was found that these could be expressed as

$$\left.\begin{aligned} \left\{ V_n + \sum_{n'} \left(\tfrac{1}{2} \overline{q_{n'}^2}\right) V_{nn'n'} \right\} &= 0 \\ \left\{ \tilde{V}_{nn'} + \sum_{n''} \left(\tfrac{1}{2} \overline{q_{n''}^2}\right) V_{nn'n''n''} \right\} &= 0 \end{aligned}\right\}. \qquad (2.13)$$

It will also be shown in chapter 3 that the formula for $\mathcal{F}$ to be derived from (1.21) and (2.11) has these conditions (2.13) as the solution, to the present approximation, of minimum conditions $\frac{\partial \mathcal{F}}{\partial p} = 0$, where p represents in turn each of the parameters of chapter 1: the differentiation of the first part of $\mathcal{F}$ arising from the known $\overline{O_n^{(2)}}$ of (2.3) changes the numerical factors in such a way as just to reproduce the curly brackets of (2.11).

These two other approaches are consistent with our writing $\overline{\Delta_\omega}$ as in (2.11); it then follows that if the adaptation of the oscillators (which is the choice of the parameters x_ℓ^{neq}, $e_{\ell\omega}$, ω_ω) is made by solving the equations (2.13), these "adaptation conditions" will have (approximately) the two physical interpretations given above. There are just as many equations as there are unknowns.

2b: Their Solution.

We have to solve simultaneously the equations

$$V_\omega + \sum_{\omega'} \chi_{\omega'} V_{\omega\omega'\omega'} = 0 \quad , \quad \omega = 1 \dots 3N ,$$

$$\tilde{V}_{\omega\omega} + \sum_{\omega'} \chi_{\omega'} V_{\omega\omega\omega'\omega'} = 0 \quad , \quad \omega = 1 \dots 3N , \tag{2.13'}$$

$$V_{\omega\omega'} + \sum_{\omega''} \chi_{\omega''} V_{\omega\omega'\omega''\omega''} = 0 \quad , \quad \omega \neq \omega' = 1 \dots 3N ,$$

where we write

$$\chi_\omega = \tfrac{1}{2} \overline{q_\omega^2} = \frac{1}{2} \frac{E_\omega}{\omega_\omega} \left(\to \frac{1}{4} \frac{t_\omega}{\omega_\omega} \text{ as } T \to 0 \right) \tag{2.14}$$

for short ($\tilde{V}_{\omega\omega'} = V_{\omega\omega'}$, $\omega \neq \omega'$, by (1.13)). Two

cases will be distinguished; the "perturbation case", in which the third and fourth degree terms are to be regarded as small corrections -- this was outlined by Born (1951a)-- and the "non-linear case", in which all terms are of equal importance -- this is so for solid helium, and an approximation to the solution will form the basis for the application of the theory in chapter 7.

We may first transcribe (2.13) using (1.5) and (1.13):

$$u_\ell + \sum_{\ell'\ell''} u_{\ell\ell'\ell''} A_{\ell'\ell''} = 0 , \tag{2.15}$$

$$\sum_{\ell\ell'} \frac{e_{\ell n} e_{\ell' n'}}{\sqrt{m_\ell m_{\ell'}}} \left\{ u_{\ell\ell'} + \sum_{\ell''\ell'''} u_{\ell\ell'\ell''\ell'''} A_{\ell''\ell'''} \right\} = \delta_{nn'} \omega_n^2 , \tag{2.16}$$

where

$$A_{\ell_1\ell_2} = \sum_n \chi_n \frac{e_{\ell_1 n} e_{\ell_2 n}}{\sqrt{m_{\ell_1} m_{\ell_2}}} . \tag{2.17}$$

The perturbation case[+] then has as its zero-order solution

$$\left.\begin{aligned} u_\ell &= 0 \\ \sum_{\ell\ell'} \frac{u_{\ell\ell'}}{\sqrt{m_\ell m_{\ell'}}} e^0_{\ell n} e^0_{\ell' n'} &= \delta_{nn'} \omega_n^{0\,2} \end{aligned}\right\} , \tag{2.18}$$

+ We write ^{0} , ^{1} , ^{2} ,... for the successive orders; this is of course not the perturbation W , which does not appear again.

which defines the usual $x_\ell^{ref\,0}$, $e_{\ell m}^0$, ω_m^0 of the harmonic theory -- the reference positions define a minimum configuration of the static potential energy, about which small vibrations have the frequencies ω_ℓ^0, the roots of the dynamical matrix $D_{\ell\ell'}^0 = \dfrac{u_{\ell\ell'}}{\sqrt{m_\ell m_{\ell'}}}$. This is the solution $H=H^0$, $v_i^0 = 0$ of chapter 1. The functions $u, A, \ldots$ which appear in the perturbation formulae are all to be understood as having these $x_\ell^{ref\,0}, e_{\ell m}^0, \omega_m^0$ for their arguments.

The first order solution of (2.15) is

$$\left.\begin{aligned} \sum_{\ell'} u_{\ell\ell'}\, x_{\ell'}^{ref\,1} &= -\sum_{\ell_1\ell_2} u_{\ell\ell_1\ell_2} A_{\ell_1\ell_2} \\ x_\ell^{ref\,1} &= -\sum_{\ell'} (u^{-1})_{\ell\ell'} \sum_{\ell_1\ell_2} u_{\ell'\ell_1\ell_2} A_{\ell_1\ell_2} \end{aligned}\right\}, \tag{2.19}$$

the reciprocal matrix $(u^{-1})_{\ell\ell'}$ being defined by

$$(u^{-1})_{\ell\ell'} = \sqrt{m_\ell m_{\ell'}} \sum_m \frac{e_{\ell m} e_{\ell' m}}{\omega_m^2}, \tag{2.20}$$

the sum being extended over all non-vanishing frequencies (to avoid translations as mentioned above). This provides vibrational corrections to the reference positions, even at $T = 0^\circ K$.

The corresponding solution of (2.16) is got by the well-known perturbation procedure applied to a set of characteristic equations: if we write $D^{0}_{\ell\ell'}$, as above, and $D^{1}_{\ell\ell'}$ as

$$D^{1}_{\ell\ell'} = \frac{1}{\sqrt{m_\ell m_{\ell'}}} \left\{ \sum_{\ell''} u_{\ell\ell'\ell''} x^{0}_{\ell''} + \sum_{\ell''\ell'''} u_{\ell\ell'\ell''\ell'''} A_{\ell''\ell'''} \right\}$$

$$= \frac{1}{\sqrt{m_\ell m_{\ell'}}} \sum_{\ell_1\ell_2} \left\{ u_{\ell\ell'\ell_1\ell_2} - u^{(3)}_{\ell\ell'\ell_1\ell_2} \right\} A_{\ell_1\ell_2} , \tag{2.21}$$

where, by (2.19),

$$u^{(3)}_{\ell\ell'\ell_1\ell_2} = \sum_{\ell''\ell'''} u_{\ell\ell'\ell''} \left(\alpha^{-1}\right)_{\ell''\ell'''} u_{\ell'''\ell_1\ell_2} , \tag{2.22}$$

we have to solve

$$\sum_{\ell\ell'} \left(D^{0}_{\ell\ell'} + D^{1}_{\ell\ell'} \right) e_{\ell m} e_{\ell' m'} = \delta_{mm'} \omega_m^2 ;$$

the result is

$$\omega_n^1 = \frac{1}{2\omega_n^0} \sum_{ll'} D_{ll'}^1 e_{ln}^0 e_{l'n}^0 ,$$

$$e_{ln}^1 = \sum_{n'}{}' e_{ln'}^0 \left\{ \frac{\sum_{l'l''} D_{l'l''}^1 e_{l'n'}^0 e_{l''n}^0}{\omega_n^{0\,2} - \omega_{n'}^{0\,2}} \right\} \Bigg\} .$$

(2.23)

(It may be noted that $\sum_l e_{ln}^0 e_{ln}^1 = 0$).
This provides corrections to the usual harmonic frequencies: the first part of $D_{ll'}^1$ arises from the expanded reference positions, the second part is the direct effect of fourth degree terms.

The formulation of these perturbation results is due to Professor Born; he has suggested to call the $x_l^{\alpha\,1}$ the thermal displacements, due to thermal forces $\mathfrak{F}_l = \sum_{l_1 l_2} U_{l l_1 l_2} A_{l_1 l_2}$ (discussed further by him in regard to a lattice configuration in the paper already quoted (1951a)), and the e_{ln}^1 , ω_n^1 the thermal agitation; in both cases the temperature dependence is given through the factor $A_{l_1 l_2}$, a function of the vibrational energies E_n . An illustration

of this method will be given in chapter 5, where the linear chain is considered; the method is appropriate to the case when quantum effects are small.

In the non-linear case, as applied to solid helium, we shall be concerned with the vibrational equations alone. If we assume as a trial solution for the positions x_l^{eq} a regular Bravais lattice configuration then the first (position) equation of (2.13') can be shown to hold identically; for the lattice parameters are not determined and may be got by applying minimum conditions to the free energy: these points are illustrated by the linear-chain example in chapter 5. The large vibrational energy is the main influence in the properties of a strongly anharmonic solid, and we shall require a "non-linear" solution of the second (frequency) equation in (2.13') to give new ω_λ ; it will be made to correspond with the usual helium lattice configuration, and it does not matter very much what other possible exact reference positions there are.

The equation (2.16) involves the product of four factors $e_{l\lambda}$ in any exact solution -- this is the non-linear problem. However, we may write the non-diagonal part as

$$\sum_{ll'} \frac{e_{l\lambda_1} e_{l'\lambda_2}}{\sqrt{m_l m_{l'}}} u_{ll'} \left\{ 1 + \sum_{l''l'''} A_{l''l'''} \frac{u_{ll'l''l'''}}{u_{ll'}} \right\}_{\lambda_1 \neq \lambda_2} = 0, \qquad (2.24)$$

and if the ratio $\frac{u_{ll'l''l'''}}{u_{ll'}}$, or the $\sum_{l''l'''}$

containing it, were largely independent of l, l' we would have

$$\sum_{ll'} \frac{e_{\ell n_1} e_{l' n_2}}{\sqrt{m_\ell m_{l'}}} u_{ll'} \sim 0 , \tag{2.25}$$

the usual non-diagonal equations for the $e^0_{\ell n}$. We shall here assume that the approximation (2.25) can be used instead of (2.24) with sufficient accuracy: this defines the $e_{\ell n}$ as the usual $e^0_{\ell n}$ of the harmonic theory, and implies both the non-diagonal relations

$$V_{n_1 n_2} = 0 \quad , \; n_1 \neq n_2 ,$$

and the diagonal relations

$$V_{nn} = \omega_n^{0\,2} \; ;$$

the diagonal $\omega_n^{0\,2}$ may have any value, positive, negative, or zero (the square being written for convenience).

The third set of (non-diagonal) equations in (2.13') is then accounted for; but now the diagonal equations from (2.13') remain to determine the new frequencies ω_n,

$$\omega_n^2 = \omega_n^{0\,2} + \sum_{n'} \chi_{n'} V_{nn'n'n} \; : \tag{2.26}$$

the simultaneous conditions for e_{ll} , ω_l have been replaced by first approximating to the non-diagonal $e_{ll'}$ conditions, then using the result in the physically more essential diagonal frequency equations, and this method will hereafter be referred to as the "non-linear solution". It allows us to consider generalised normal modes of vibration, governed by the fourth degree terms in the potential; they constitute waves of exactly the same form as the usual normal modes, but having different frequencies. This approximation seems to be quite sufficient for the present helium application.

The equations (2.26) immediately express each ω_l^2 in terms of the sum of the energies of them all:

$$\omega_l^2 = \omega_l^{0\,2} + \tfrac{1}{2}\sum_{l'} \frac{E_{l'}}{\omega_{l'}^2} V_{llll'l'} \;; \qquad (2.26')$$

this kind of relationship will be discussed further in chapter 4. For solid helium the zero energy is of most importance, being some 10 times the average thermal energy, and (2.26') becomes approximately

$$\omega_l^2 = \omega_l^{0\,2} + \frac{\hbar}{4}\sum_{l'} \frac{V_{llll'l'}}{\omega_{l'}} \;. \qquad (2.27)$$

this form of the equation will be used in chapter 5 to obtain an exact solution for the linear chain. Again, at about fcc molar volume, the harmonic frequencies $\omega_k^{0\,2} \sim 0$ for solid helium (see chapter 6), and in that case ω_k^2 depends directly on the fourth degree terms,

$$\omega_k^2 = \frac{1}{2} \sum_{k'} \frac{E_{k'}'}{\omega_{k'}^2} V_{kkk'k'} : \qquad (2.28)$$

this is also illustrated in chapter 5. In all these cases it should be remembered that $e_{\ell\ell'}^0$ is to be used, and the equations (2.26'), (2.27) may then be solved by iteration; this will not be done here, as the corresponding solutions of the linear chain can be used to provide a sufficient basis for the helium application.

CHAPTER 3: THERMODYNAMICAL DEVELOPMENT.

3a: The Free Energy.

The general formula for $\mathcal{F}$ proposed in chapter 1 is

$$\mathcal{F} = \mathcal{U}_0 + F + \overline{\Delta_m}, \tag{3.1}$$

where F is the free energy of the system of independent oscillators,

$$F = kT \sum_{n}^{(3N)} \log\left\{2\sinh\left(\tfrac{1}{2}h\nu_n/kT\right)\right\}, \tag{3.2}$$

and, by (2.11), (2.14), $\overline{\Delta_m}$ is given in full by

$$\begin{aligned}\overline{\Delta_m} = {} & \sum_n \lambda_n \tilde{V}_{nm} + \tfrac{1}{2!}\sum_{nn'} \lambda_n\lambda_{n'} V_{nmn'm} \\ & - \sum_n \frac{\lambda_n}{E_{0n}}\left\{V_{nm} + \sum_{n'} \lambda_{n'} V_{nmn'm}\right\}^2 \\ & - \tfrac{1}{2!}\sum_{nn'} \frac{\lambda_n\lambda_{n'}}{\frac{1}{2}(E_{0n}+E_{0n'})}\left\{\tilde{V}_{nn'} + \sum_{n''} \lambda_{n''} V_{nmn'n''}\right\}^2,\end{aligned} \tag{3.3}$$

small second and higher order terms being neglected. In the non-linear case the adaptation conditions proposed in chapter 2 reduce this last expression to

$$\overline{\Delta}_n = \frac{1}{2}\sum_h \lambda_h \tilde{V}_{hh} = -\frac{1}{2}\sum_{hh'} \lambda_h \lambda_{h'} V_{hh'h'h}, \tag{3.4}$$

to the same degree of approximation. In the perturbation case, the successive approximate solutions of (2.13') should be paralleled by a development of (3.1) - (3.3) in successive approximations during which the squared brackets and higher order terms automatically drop out: this expansion, due to Born, is given below.

Before developing these results it is of interest to notice that the same adaptation conditions satisfy, to the present degree of approximation, minimum conditions on the free energy. If we regard the foregoing expression (3.1) - (3.3) for $\mathcal{F}$ as a function of the $6N + \frac{1}{2}3N(3N-1)$ variables x_ℓ^{ref} , ω_h , $e_{\ell h}$, then we may set up the minimum conditions

$$\left.\begin{aligned} &\frac{\partial \mathcal{F}}{\partial x_\ell^{ref}} = 0 \quad , \quad \ell = 1 \ldots 3N \\ &\frac{\partial \mathcal{F}}{\partial \omega_h} = 0 \quad , \quad h = 1 \ldots 3N \end{aligned}\right\} \tag{3.5}$$

$$\sum_\ell \left(\frac{\partial \mathcal{F}}{\partial e_{\ell h_1}} e_{\ell h_2} - \frac{\partial \mathcal{F}}{\partial e_{\ell h_2}} e_{\ell h_1} \right) = 0 \quad , \quad h_1 \neq h_2 = 1 \ldots 3N$$

to determine them; there are just sufficient independent equations to do this. The form of the equations in $e_{\ell m}$ arises from the additional orthogonality conditions (1.4) which they must satisfy: introducing Lagrangian multipliers we may write+

$$\mathcal{F}^* = \mathcal{F} + \tfrac{1}{2}\sum_{mm'} \mu_{mm'}\left(\sum_{\ell} e_{\ell m} e_{\ell m'} - \delta_{mm'}\right),$$

with $\mu_{mm'} = \mu_{m'm}$, and impose the conditions

$$\frac{\partial \mathcal{F}^*}{\partial e_{\ell m_1}} = \frac{\partial \mathcal{F}}{\partial e_{\ell m_1}} + \sum_{m} \mu_{m_1 m} e_{\ell m} = 0,$$

$$\frac{\partial \mathcal{F}^*}{\partial e_{\ell m_2}} = \frac{\partial \mathcal{F}}{\partial e_{\ell m_2}} + \sum_{m} \mu_{m_2 m} e_{\ell m} = 0.$$

+ The alternative set of orthogonality relations

$$\sum_{m} e_{\ell m} e_{\ell' m} - \delta_{\ell\ell'} = 0$$

can not be used here, since the conditions to which they lead,

$$\sum_{m}\left(\frac{\partial \mathcal{F}}{\partial e_{\ell m}} e_{\ell' m} - \frac{\partial \mathcal{F}}{\partial e_{\ell' m}} e_{\ell m}\right) = 0,$$

would have to include those m for which $\omega_m = 0$: these translations have always to be omitted (as can be done) from the $\sum_m$ which may occur, to avoid divergences.

Multiplying the first of these by $e_{\ell n_2}$, the second by $e_{\ell n_1}$, and adding over ℓ, we find

$$\left.\begin{aligned} \sum_\ell \frac{\partial \mathcal{F}}{\partial e_{\ell n_1}} e_{\ell n_2} + \mu_{n_1 n_2} &= 0 \\ \sum_\ell \frac{\partial \mathcal{F}}{\partial e_{\ell n_2}} e_{\ell n_1} + \mu_{n_1 n_2} &= 0 \end{aligned}\right\} . \qquad (3.6)$$

Subtracting, for $n_1 \neq n_2$, we have

$$\sum_\ell \left(\frac{\partial \mathcal{F}}{\partial e_{\ell n_1}} e_{\ell n_2} - \frac{\partial \mathcal{F}}{\partial e_{\ell n_2}} e_{\ell n_1} \right) = 0,$$

as quoted in (3.5); the diagonal μ_{nn} -- defined directly by either of (3.6) -- are irrelevant here.

The first of the equations (3.5), applied to (3.1) - (3.3), gives

$$\begin{aligned} \frac{\partial \mathcal{F}}{\partial x_\ell^{\alpha\dagger}} \equiv & \left\{ u_\ell + \sum_{\ell_1 \ell_2} u_{\ell\ell_1\ell_2} A_{\ell_1\ell_2} \right\} \\ & - 2 \sum_n \frac{\lambda_n}{E_{0n}} \left\{ V_n + \sum_{n'} \lambda_{n'} V_{nn'n'} \right\} . \\ & \cdot \sum_{\ell'} \frac{e_{\ell' n}}{\sqrt{m_{\ell'}}} \left(u_{\ell\ell'} + \sum_{\ell''\ell'''} u_{\ell\ell'\ell''\ell'''} A_{\ell''\ell'''} \right) \\ & - \sum_{nn'} \frac{\lambda_n \lambda_{n'}}{\frac{1}{2}(E_{0n} + E_{0n'})} \left\{ \tilde{V}_{nn'} + \sum_{n''} \lambda_{n''} V_{nn'n''n''} \right\} \left\{ \text{terms in } u_{\ell\ell'\ell''} \right\} \\ & + \cdots = 0, \end{aligned}$$

where the definitions (1.5) have been used;
adding for all ℓ, we have

$$\sum_\ell \frac{e_{\ell n}}{\sqrt{m_\ell}} \frac{\partial \mathcal{E}}{\partial x_{\ell q}} \equiv \left\{ V_n + \sum_{n'} \lambda_{n'} V_{nn'n'} \right\}$$

$$- 2 \sum_{n'} \frac{\lambda_{n'}}{\epsilon_{0n'}} \left\{ V_{n'} + \sum_{n''} \lambda_{n''} V_{n'n'n''} \right\} \cdot$$

$$\cdot \left\{ \tilde{V}_{nn'} + \sum_{n''} \lambda_{n''} V_{nn'n''n''} \right\}$$

$$- \sum_{n'n''} \frac{\lambda_{n'} \lambda_{n''}}{\frac{1}{2}(\epsilon_{0n'} + \epsilon_{0n''})} \left\{ \tilde{V}_{n'n''} + \sum_{n'''} \lambda_{n'''} V_{n'n''n'''n'''} \right\} \left\{ \text{terms in } V_{nn'n''} \right\}$$

$$+ \cdots \cdot$$

$$= 0 \,.$$

(3.7)

It is clear that this can be satisfied by taking

$$\left\{ V_n + \sum_{n'} \lambda_{n'} V_{nn'n'} \right\} = 0 \,, \qquad n = 1 \ldots 3N,$$

$$\left\{ \tilde{V}_{nn} + \sum_{n'} \lambda_{n'} V_{nnn'n'} \right\} = 0 \,, \qquad n = 1 \ldots 3N,$$

$$\left\{ \tilde{V}_{nn'} + \sum_{n''} \lambda_{n''} V_{nn'n'n''} \right\} = 0 \,, \qquad n \neq n' = 1 \ldots 3N,$$

just the three conditions (2.13'); here any

additional small terms in (3.7) are neglected.

When we bear in mind the oscillator relations

$$2\lambda_n = \bar{q}_n^2 = \frac{E_n}{\omega_n^2}, \tag{3.8}$$

$$E_n = \tfrac{1}{2}\hbar\omega_n \coth\left(\tfrac{1}{2}\hbar\omega_n/kT\right) = \tfrac{1}{2}\hbar\omega_n + kT\,P(\hbar\omega_n/kT), \tag{3.9}$$

(E_n being the mean vibrational energy, zero energy $\tfrac{1}{2}\hbar\omega_n$ plus Planck energy), and the definition (1.13) for $\tilde{V}_{nn'}$, $\tilde{V}_{nn'} = V_{nn'} - \omega_n^2\delta_{nn'}$, we can readily show that the second of equations (3.5) is

$$\frac{\partial \mathcal{F}}{\partial \omega_n} \equiv \frac{\partial \lambda_n}{\partial \omega_n}\left\{\tilde{V}_{nn} + \sum_{n'}\lambda_{n'}V_{nnn'n'}\right\}$$

$$-\sum_{n'}\left[\frac{\partial}{\partial\omega_n}\left(\frac{\lambda_n\lambda_{n'}}{\tfrac{1}{2}(E_{0n}+E_{0n'})}\right)\left\{\tilde{V}_{nn'} + \sum_{n''}\lambda_{n''}V_{nnn''n''}\right\}^2\right.$$

$$\left. + \delta_{nn'}\frac{\partial}{\partial\omega_n}\left(\frac{\lambda_n}{E_{0n}}\right)\cdot\left\{V_{nn} + \sum_{n''}\lambda_{n''}V_{nnn''n''}\right\}^2\right]$$

$$-\left[\text{terms linear in the } \{\ \} \text{ brackets}\right]$$

$$+ \cdots$$

$$= 0, \tag{3.10}$$

the terms in square brackets all containing one or other of the adaptation expressions in (2.13'). Again, the equations (2.13') satisfy the minimum condition.

Finally, the last of (3.5) leads to the expression

$$\sum_{\ell} e_{\ell\alpha\nu} \frac{\partial \mathcal{F}}{\partial \ell_{\alpha\nu_1}} \equiv 2\lambda_{\nu_1} \left\{ \tilde{V}_{\nu_1\nu_2} + \sum_{\nu} \lambda_{\nu} V_{\nu_1\nu_2\nu\nu} \right\}$$

$$- 2\lambda_{\nu_1} \left[\sum_{\nu} \frac{\lambda_{\nu}}{\epsilon_{0\nu}} \left\{ V_{\nu\nu} + \sum_{\nu'} \lambda_{\nu'} V_{\nu\nu\nu'\nu'} \right\} \{ \cdots \} \right.$$

$$\left. + \frac{1}{2!} \sum_{\nu\nu'} \frac{\lambda_{\nu}\lambda_{\nu'}}{\frac{1}{2}(\epsilon_{0\nu}+\epsilon_{0\nu'})} \left\{ \tilde{V}_{\nu\nu\nu'} + \sum_{\nu''} V_{\nu\nu\nu'\nu''} \lambda_{\nu''} \right\} \{ \cdots \} \right],$$

$$+ \cdots \cdots$$

so that

$$\sum_{\ell} \left(e_{\ell\alpha\nu} \frac{\partial \mathcal{F}}{\partial \ell_{\alpha\nu_1}} - e_{\ell\alpha\nu} \frac{\partial \mathcal{F}}{\partial \ell_{\alpha\nu_2}} \right) \equiv$$

$$2(\lambda_{\nu_1} - \lambda_{\nu_2}) \left[\left\{ \tilde{V}_{\nu_1\nu_2} + \sum_{\nu} \lambda_{\nu} V_{\nu_1\nu_2\nu\nu} \right\} \right.$$

$$- \sum_{\nu} \frac{\lambda_{\nu}}{\epsilon_{0\nu}} \left\{ V_{\nu\nu} + \sum_{\nu'} \lambda_{\nu'} V_{\nu\nu\nu'\nu'} \right\} \{ \cdots \}$$

$$\left. - \frac{1}{2!} \sum_{\nu\nu'} \frac{\lambda_{\nu}\lambda_{\nu'}}{\frac{1}{2}(\epsilon_{0\nu}+\epsilon_{0\nu'})} \left\{ \tilde{V}_{\nu\nu\nu'} + \sum_{\nu''} V_{\nu\nu\nu'\nu''} \right\} \{ \cdots \} \right] \tag{3.11}$$

$$+ \cdots \cdots$$

$$= 0 ,$$

where again the omitted terms are either small or go with the adaptation expressions (2.13'). Since in this equation $k_1 \neq k_2$ [+], we have

$$\left\{\tilde{V}_{k_1 k_2} + \sum_n \lambda_{kn} V_{k_1 k_2 kn}\right\} - \sum_n \frac{\lambda_{kn}}{E_{0n}} \left\{V_{kn} + \sum_{k'} \lambda_{k'n} V_{k_1 k_2 k' k}\right\}\{\cdots\} - \frac{1}{2!}\sum_{kk'} \cdots = 0,$$

which again is satisfied by the adaptation conditions.

In the perturbation case, these minimum conditions can be solved simultaneously by successive approximations: the results are then, at each stage, quite the equivalent of the perturbation solution outlined in chapter 2, and this completes the min-max approach to the conditions (2.13') mentioned there.

For a regular lattice, in which (2.15) is

+ The restriction $k_1 \neq k_2$ does not not preclude the possibility of $\lambda_{k_1} = \lambda_{k_2}$, or $\omega_{k_1}^2 = \omega_{k_2}^2$, as is to be expected for various sets of frequencies in a lattice spectrum: in that case the minimum condition is identically zero, and the corresponding condition

$$\left\{\tilde{V}_{k_1 k_2} + \sum_n \lambda_{kn} V_{k_1 k_2 kn}\right\}$$

must be specified otherwise.

identically fulfilled, it is a natural extension of this method to solve for the lattice parameters by minimum conditions $\partial \mathcal{F}/\partial a_{\alpha\beta} = 0$. This will be illustrated for a one-dimensional model in chapter 5, where the non-linear and perturbation cases are contrasted; the general lattice solutions are in principle the same.

The expansion of $\mathcal{F}$ by successive approximations consists in writing

$$\mathcal{F} = \mathcal{F}^0 + \mathcal{F}^1 + \mathcal{F}^2 ,$$

where

$$\mathcal{F}^0 = U_0 ,$$

$$\mathcal{F}^1 = \sum_l U_l x_l^{\alpha\beta 1} + F^0 + \sum_n \lambda_n \tilde{V}_{nn} ,$$

$$\mathcal{F}^2 = \sum_l U_l x_l^{\alpha\beta 2} + F^1 + \frac{1}{2!} \sum_{ll'} U_{ll'} x_l^{\alpha\beta 1} x_{l'}^{\alpha\beta 1} + \sum_n \left(\lambda_n \tilde{V}_{nn}\right)^1 + \frac{1}{2!} \sum_{nn'} \lambda_n \lambda_{n'} V_{nnn'n'} ,$$

(3.12)

the arguments of the various functions being the zero and first order solutions of the adaptation conditions,

$$\left.\begin{aligned} x_\ell^{eq} &= x_\ell^{eq\,0} + x_\ell^{eq\,1} + \cdots \\ \omega_h &= \omega_h^0 + \omega_h^1 + \cdots \\ e_{\ell h} &= e_{\ell h}^0 + e_{\ell h}^1 + \cdots \end{aligned}\right\} ;$$

when no superscript appears the arguments are the

$x_\ell^{eq\,0}$, $e_{\ell h}^0$, ω_h^0

given by (2.18). This being similar to the usual harmonic theory, the vibrational terms are regarded as small compared to the static potential u_0. From the results of chapter 2 and the work of the previous paragraphs it can be readily shown that

$$\begin{aligned} \mathcal{F}^0 &= u_0\left(x_\ell^{eq\,0}\right), \\ \mathcal{F}^1 &= kT\sum_h \log\left\{2\sinh\left(\tfrac{1}{2}\hbar\omega_h^0/kT\right)\right\}, \\ \mathcal{F}^2 &= \mathcal{F}^2_{(3)} + \mathcal{F}^2_{(4)} , \end{aligned} \qquad (3.13)$$

where $\mathcal{F}^2_{(3)}$, $\mathcal{F}^2_{(4)}$ are the contributions from the third and fourth degree terms in the potential:

$$\mathcal{F}^2_{(3)} = -\tfrac{1}{2!}\sum_{\ell_1\ell_2\ell_3\ell_4} A_{\ell_1\ell_2} A_{\ell_3\ell_4}\, u^{(3)}_{\ell_1\ell_2\ell_3\ell_4}, \qquad (3.14)$$

where

$$u^{(3)}_{l_1 l_2 l_3 l_4} = \sum_{ll'} u_{l_1 l_2 l} (u^{\gamma})_{ll'} u_{l' l_3 l_4} ,$$

the reciprocal quadratic matrix $(u^{\gamma})_{ll'}$ and the $A_{ll'}$ being defined by (2.20), (2.17) -- this part comes from the changed lattice positions, $x_l^{eq\,0} + x_l^{eq\,1}$;

$$\mathcal{F}^2_{(4)} = \frac{1}{2!} \sum_{l_1 l_2 l_3 l_4} A_{l_1 l_2} A_{l_3 l_4} u_{l_1 l_2 l_3 l_4} , \qquad (3.15)$$

arising from direct changes in the energy levels. These formulae will be illustrated by the linear chain example in chapter 5.

Returning to the non-linear theory, we have from (3.1) and (3.4)

$$\mathcal{F} = u_0 + F + \frac{1}{2} \sum_n \lambda_n \tilde{V}_{nn}$$

$$= u_0 + F - \frac{1}{4} \sum_n E_n + \frac{1}{4} \sum_n E_n \frac{V_{nn}}{\omega_n^2}$$

$$= u_0 + F - \frac{1}{4} E + \frac{1}{4} \sum_n E_n f_{nn} , \qquad (3.16)$$

where F , E are the free energy and internal energy of the adapted system of independent oscillators, and f_n is the ratio of the squared frequency of the n^{th} normal mode of vibration as given by the usual harmonic theory,

$$V_{nn} = \omega_n^{0\,2}, \qquad (e_{en} \equiv e_{en}^0 \text{ is chosen}),$$

which may be zero or negative, to the squared frequency of the n^{th} adapted harmonic mode based on the terms of fourth degree in V . This ratio,

$$f_n = \frac{\omega_n^{0\,2}}{\omega_n^{\,2}}, \qquad (3.17)$$

describes the non-linearity of the new theory: when $f_n \to 1$, the usual results become applicable, and the last two terms of (3.16) cancel leaving the normal expression for F . As $T \to 0$, (3.16) reduces to

$$F_0 = U_0 + \varepsilon_0,$$

where the zero-energy ε_0 is

$$\varepsilon_0 = \tfrac{1}{4} \sum_n \left(\tfrac{1}{2} h\nu_n\right)(3 + f_n). \qquad (3.18)$$

In the particular case when $V_{nn} = \omega_n^{o\,2} \sim 0$, so that $f_n \sim 0$ (e.g. for solid helium near 14 cc / mole), ω_n is given by (2.28), and we may write

$$\mathcal{F} \sim u_0 + F - \tfrac{1}{4}E ,$$

and at low temperatures

$$\mathcal{E}_0 \sim \tfrac{3}{2}\sum_{nn'} \lambda_n \lambda_{n'} V_{nnn'n'} = \tfrac{3}{2}\sum_{n_1 n_2 n_3 n_4} A_{n_1 n_2} A_{n_3 n_4} u_{n_1 n_2 n_3 n_4} . \tag{3.19}$$

3b: Non-linear Thermodynamical Properties.

For the non-linear theory we may apply the usual thermodynamical relations to the formula (3.16) for $\mathcal{F}$. We then have the entropy ($\mathcal{S}$), internal energy ($\mathcal{E}$), and specific heat at constant volume ($\mathcal{C}$)[+] given by

$$\mathcal{S} = -\left(\frac{\partial \mathcal{F}}{\partial T}\right)_v = S + \tfrac{1}{4}C - \tfrac{1}{4}\sum_n C_n f_n , \tag{3.20}$$

$$\mathcal{E} = \mathcal{F} + T\mathcal{S} = u_0 + \tfrac{3}{4}E + \tfrac{1}{4}TC + \tfrac{1}{4}\sum_n (E_n - TC_n) f_n \tag{3.21}$$

[+] Since only constant volume is considered we will omit the usual suffix v in this context.

$$b_v = \left(\frac{\partial \mathcal{E}}{\partial T}\right)_v = C_v + \frac{1}{4}T\left(\frac{\partial C}{\partial T}\right)_v - \frac{1}{4}\sum_\omega T\left(\frac{\partial C_\omega}{\partial T}\right)_v f_\omega , \quad (3.22)$$

where S , $\mathcal{E}$, C_v are the corresponding oscillator quantities, which are well-known.

We shall assume the reference system x_e^{neq} to define a regular lattice+ and evaluate these expressions with the help of the isotropic Debye approximation, discussed in the next chapter. It will be shown there that we may apply the usual continuum approximation to the adapted harmonic spectrum++ of vibrations, the density of vibrational modes in each of the three acoustic branches being written

$$dz = \frac{3N\omega^2 d\omega}{\omega_D^3} = \frac{3N\,\xi^2\,d\xi}{x^3} , \quad (3.23)$$

where ω_D is Debye's isotropic maximum frequency (see (4.23), (4.24)) and

$$\xi = \frac{\hbar\omega}{kT} ,$$

$$x = \frac{\Theta}{T} , \quad (3.24)$$

$$\Theta = \frac{\hbar\omega_D}{k} \text{ +++} .$$

++ We consider only a monatomic lattice, the application being to solid helium in the following chapters.

+++ We shall write for short Θ , x as the elastically defined quantities of the next chapter instead of Θ_D , x_D as used there.

+ We may write Φ instead of $\mathcal{U}$ in this case.

We shall not develop the more general formulae without the isotropic assumption (i.e. with separate limits x_j to each branch) since the present approximation will be shown in chapter 7 to give perfectly adequate results. In the usual manner the free energy (3.2) of the system of oscillators becomes

$$F = 3RT\frac{3}{x^3}\int_0^x \left\{\tfrac{1}{2}\xi + \log(1-e^{-\xi})\right\}\xi^2 d\xi$$

$$= \frac{9}{8}R\Theta - RTD(x) + 3RT\log(1-e^{-x}), \tag{3.25}$$

where $D(x)$ is Debye's function

$$D(x) = \frac{3}{x^3}\int_0^x P(\xi)\xi^2 d\xi = \frac{3}{x^3}\int_0^x \frac{\xi^3 d\xi}{e^{\xi}-1}. \tag{3.26}$$

The entropy S is then well-known to be

$$S = 4RD(x) - 3R\log(1-e^{-x});$$

the internal energy is

$$E = \frac{9}{8}R\Theta + 3RTD(x); \tag{3.27}$$

the specific heat at constant volume is

$$C = 3R\left\{4D(x) - 3P(x)\right\}, \qquad (3.28)$$

$P(x)$ being Planck's function

$$P(x) = \frac{x}{e^x - 1} . \qquad (3.29)$$

The remaining terms containing the ratio f_h can also be handled with the Debye integral. For a lattice we should write the wave-vector index h as $\binom{h}{j}$, where $(h) = (h_1, h_2, h_3)$ is a point of reciprocal space as will be defined in chapter 4, and j denotes the branch of the lattice spectrum -- we are interested here in the three acoustic branches $j = 1, 2, 3$. By the formula (2.26) of the preceding chapter we may write

$$f\binom{h}{j} = 1 - \frac{1}{2}\frac{1}{\omega\binom{h}{j}^2}\sum_{\binom{h'}{j'}} \frac{E\binom{h'}{j'}}{\omega\binom{h'}{j'}^2} V\left(\begin{matrix} h & h & h' & h' \\ j & i & j' & j' \end{matrix}\right); \qquad (3.30)$$

for each branch of the spectrum (j fixed) f is a function of (h). We may define a corresponding function of ω by means of the relation

$$f_j(\omega) = \frac{d}{d\omega} \iiint_{0<\omega(\mathbf{h})<\omega} f(\mathbf{h}_j)\, d(\mathbf{h}) \Big/ \frac{d}{d\omega} \iiint_{0<\omega(\mathbf{h})<\omega} d(\mathbf{h}) \quad , \tag{3.31}$$

this being an average value of the $f(\mathbf{h}_j)$ at those points $(\mathbf{h})$ of reciprocal space for which the corresponding frequencies[+] $\omega(\mathbf{h}_j)$ lie within the range $\omega \to \omega+d\omega$. Reckoning now the density of frequencies in each branch according to the isotropic Debye continuum (3.23), we can replace any of the quantities

$$\sum_{(\mathbf{h}_j)} q\{\omega(\mathbf{h}_j)\} f(\mathbf{h}_j)$$

in (3.20) - (3.22) by integrals $\frac{3N}{\omega_D^3} \int_0^{\omega_D} \left(\sum_j f_j(\omega)\right) q(\omega)\, \omega^2 d\omega$; defining an average $\bar{f}(\omega)$ over the three branches, we have finally

$$\sum_{\mathbf{h}} f_{\mathbf{h}} \cdots \longrightarrow \frac{9N}{x^3} \int_0^x \bar{f}(\xi)\, \xi^2 d\xi \cdots . \tag{3.32}$$

Of course the integration of (3.31) is in practice formidable, and it will not be discussed further

+ We expect that the symmetry of the lattice, appearing now through the fourth degree terms of the potential, will make various parts of each reciprocal lattice cell (see chapter 4) equivalent in the frequencies $\omega(\mathbf{h}_j)$ they define, just as it does through the quadratic terms for the $\omega(\mathbf{h}_j)^0$.

here; it will be found in the application to solid helium that the f corresponding to the linear chain example of chapter 5 can be used as an approximation with very reasonable results. This linear chain f is in fact constant along the spectrum, f_h and $f(\omega)$ reducing to the same thing.

It should be noticed that $f(\omega)$ is also a function of the volume, $f(\omega, V)$. At each volume, the old and new frequencies will be functions of (h) as indicated schematically in fig. 3.1:

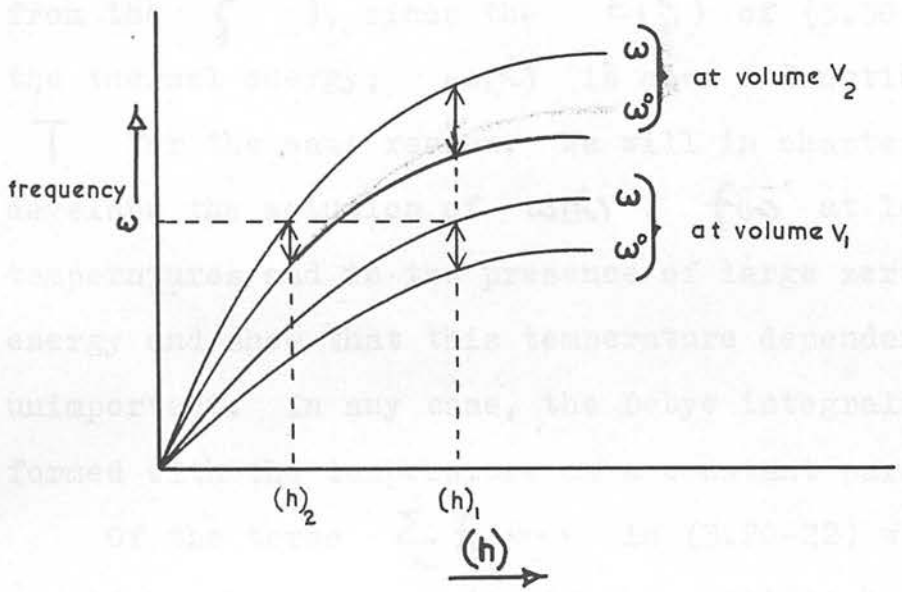


Fig. 3.1: Relation of old and new lattice frequencies.

It is clear that the same ω does not define, at different volumes, the f corresponding to the same set of points (k) of the spectrum; moreover, the f at any one point (k) is itself a function of volume. Both these dependences are covered by writing ω , V as independent variables. Moreover, in making the argument of Debye's integral $\zeta = \frac{\hbar\omega}{kT}$, we should write $f(\zeta, V, T)$, with three independent variables, to preserve f as a function of ω and V alone. Strictly speaking, f is a function of T as well as of ω and V (quite apart from the ζ), since the $\varepsilon(k_i)$ of (3.30) is the thermal energy; $\omega(k)$ is also a function of T for the same reason. We will in chapter 5 develope the solution of $\omega(k)$, $f(\omega)$ at low temperatures and in the presence of large zero energy and show that this temperature dependence is unimportant. In any case, the Debye integrals are formed with the temperature as a constant parameter.

Of the terms $\sum_k f_k \cdots$ in (3.20-22) we will consider only that arising in the specific heat formula -- the others can be treated in just the same way. We have

$$-\frac{1}{4}\sum_k T\left(\frac{\partial C_k}{\partial T}\right)_V f_k = \frac{1}{4} k \sum_k \xi_k Q(\xi_k) f_k , \qquad (3.33)$$

where

$$Q(\xi) = P(\xi) - \xi P'(\xi)$$

$$= \frac{C^E(\xi)}{3R} , \qquad (3.34)$$

the well-known Einstein specific heat function, and a dash denotes the derivative with respect to the full argument of a function. Applying the Debye integral (3.32) we get

$$-\frac{1}{4}\sum_\omega T\left(\frac{\partial C_k}{\partial T}\right)_V f_\omega \longrightarrow$$

$$\frac{9R}{4x^3}\int_0^x \bar{f}(\xi,V,T)\,Q'(\xi)\,\xi^3 d\xi$$

$$= \frac{9R}{4}\,\bar{f}(x,V,T)\left\{Q(x) - 4D(x) + 3P(x)\right\}$$

$$-\frac{9R}{4x^3}\int_0^x \frac{\partial \bar{f}}{\partial \xi}\left\{Q(\xi) - 4D(\xi) + 3P(\xi)\right\}\xi^3 d\xi .$$

We will suppose that the last term can be neglected as a result of assuming that the ratio f does not vary very greatly along any one branch of the spectrum; as mentioned above, in the linear chain example f is constant, so that this assumption is not unreasonable. The $\sum_k$ ..... term in 6 is then just

$$\frac{3}{4}\bar{f}(x,V,T)\left\{C^E(x) - C(x)\right\}, \qquad (3.35)$$

by (3.34) and (3.28).

Returning to the formula (3.22), and using (3.28), we find

$$\frac{1}{4}T\left(\frac{\partial C}{\partial T}\right)_V = -\frac{3R}{4}\left\{4x\,D'(x) - 3x\,P'(x)\right\},$$

since $\frac{dx}{dT} = -\frac{1}{T}x$; from (3.26) it is easy to show that

$$D(x) - x\,D'(x) = 4D(x) - 3P(x)$$

$$= \frac{C}{3R}, \qquad (3.36)$$

so that

$$\frac{1}{4}T\left(\frac{\partial C}{\partial T}\right)_V = -\frac{3}{4}\left\{C^E(x) - C(x)\right\}. \qquad (3.37)$$

Thus, combining (3.22), (3.35), and (3.37), we have

$$b(x,V) = C(x) - \frac{3}{4}\left\{1 - \bar{f}(x,V,T)\right\}\left\{C^E(x) - C(x)\right\}. \qquad (3.38)$$

Similar formulae could be derived for the other thermodynamical functions, but they will not be needed in what follows.

The arguments of the function $\overline{f}$ should be understood to be ω_D, the maximum Debye frequency, and V : this might be approximated by ω_m, the maximum lattice frequency, itself a function of V (no other V-dependence then arises since we stick to the end of the spectrum), and we should expect to have

$$\overline{f}(s,V,T) \sim f(\omega_m) = \frac{\omega_m^{\circ 2}}{\omega_m^2}; \qquad (3.39)$$

this is just the form of the constant f_V (for each volume) in the linear chain example of chapter 5.

CHAPTER 4 : ELASTIC THEORY.

4a: The Atomic Theory of Elasticity.

In order to discuss the elastic properties of a lattice[+] we have to set up a continuum which will be equivalent to it and defined in atomistic terms. The usual procedure takes the lattice energy Φ as providing a strain-energy-function, of which the quadratic coefficients determine the elastic constants: this has been given its most general presentation by Born (1923, 1940). On the other hand, these constants appear as coefficients in the linear elastic wave equations, which are of well-known form, and a comparison with the (linear) equations of long acoustic lattice waves yields atomistic expressions for them: this has been set out by Born and Begbie (1947).

Huang (1950) has examined the assumptions on which the latter method is based, and shown that any initial stresses must be taken to vanish before the ordinary elastic constants can be defined -- more will be said of this in 4b, where also the effect of initial stresses on the former method will be mentioned. He has also given in full the atomistic definitions when the lattice waves depend

+ We assume here the reference configuration to be a regular lattice and write Φ instead of u for the potential energy of displacement.

on the quadratic terms in the general potential function, Φ ; in the helium case they do not so that these definitions will not concern us further.

The two methods outlined above (zero initial stresses) are in agreement only so long as Φ forms the basis for each. Classically, at $T = 0^\circ K$, the lattice <u>can</u> be regarded as a static configuration from which deformations are governed by the potential energy alone, and at other temperatures the long thermal vibrations have the character of elastic waves deforming a static Φ-continuum: the agreement then follows. But at $T > 0^\circ K$ the system is a thermodynamical one to which the internal energy ε or free energy $\mathcal{F}$ is more appropriate than Φ ; if the strain-energy-density is based on either of these, while the lattice waves remain as usual defined through Φ , the two methods will <u>not</u> agree. Quantum mechanically, even at $T = 0^\circ K$ zero vibrations persist (of energy ε_0 , say), and we can never adequately picture the solid as a static Φ -continuum. At $T = 0^\circ K$ we should expect the appropriate energy density to be $\Phi + \varepsilon_0$, and at other temperatures ε or $\mathcal{F}$ as above; elastic definitions based

on these strain-energy-functions will always show some disagreement from those got by comparison with the usual lattice waves. Now even the longest lattice waves have frequencies $\sim 10^6$ sec^{-1} which ensure that the deformations they cause are adiabatic, so that we should expect $\mathcal{E}$ to provide the strain-energy-density relative to elastic wave motion; on the other hand, $\mathcal{F}$ would be appropriate to static thermodynamical elasticity -- isothermal compression, stability against shearing stress etc. -- as considered by Born (1939, 1940). In the Debye theory the velocity of elastic waves is needed in order to set up an approximation to the lattice spectrum, so that such a velocity should be adiabatically defined.

Normally the discrepancies between the static and thermodynamic definitions will be small, since in the expressions

$$\mathcal{F} = \mathcal{U} + \mathcal{E}_0 + \mathcal{F}_T \,, \tag{4.1}$$

$$\mathcal{E} = \mathcal{U} + \mathcal{E}_0 + \left(\mathcal{F}_T - T\frac{\partial \mathcal{F}_T}{\partial T}\right), \tag{4.2}$$

the terms in $\mathcal{E}_0$ and $\mathcal{F}_T$ provide small corrections; Φ can then be used to provide a strain-energy function with sufficient accuracy, and in agreement with the lattice waves. There will, of course, still be a temperature dependence of the elastic constants arising through the expansion of the lattice parameters appearing in Φ. At low temperatures, even when $\mathcal{E}_0$ is large, the thermal terms drop out, and the adiabatic and isothermal thermodynamic definitions coincide.+

The discrepancy quoted above is <u>not</u> small for helium -- for which $\mathcal{E}_0$ is on the whole larger (numerically) than Φ ; but then a new definition of lattice waves is in any case required, since the equations governing them are non-linear (large vibrations), and in fact the comparison of linear wave equations breaks down -- instead, we must compare directly the distributions of frequency with wave-number, or the velocities of long waves, in the two cases. The essential point quantum mechanically is that we can not treat one wave as existing separately from the rest. This makes the frequencies of the long acoustic lattice waves dependent on

+ For example, in solid helium at 15 cc molar volume and $10^{\circ}K$, the ratio of adiabatic to isothermal compressibilities is ~ 1.0002 , practically equal to unity.

those of the essentially coexisting shorter waves, since the energy (and so frequency) of these long waves has to do with periodic compressions of an elastic nature in which the short waves will be deformed, and their frequencies and energies altered in consequence. (it makes no difference that the long waves are (thermally) classical in character). The effect would be noticeable only in such a case as that of helium, and the new definition of lattice frequencies (chapter 2) suggests there just such a relationship. But it should also be remarked that the new definition really defines only virtual harmonic lattice waves, the real atomic vibrations being of the fourth degree. It may not be the case that the long acoustic virtual waves are identical with the harmonic adiabatic elastic waves, macroscopically defined: neither really exist in a physical sense. For helium, even at the smallest experimental molar volumes to be considered (~ 10 cc), the virtual frequency spectrum does not correspond with the harmonic spectrum as ordinarily defined (see chapter 6), and the linear-chain example (chapter 5) based on helium data does not show a close agreement between the adiabatic elastic velocity and the limiting velocity of the virtual lattice waves. On the other hand, both types of

wave do now depend properly on the large zero-energy $\mathcal{E}_0$, and are to be distinguished from waves defined through Φ. The Debye approximation in this case is needed in reference to the virtual harmonic lattice spectrum: the "elastic" velocity which specifies it ought perhaps to be chosen as the limiting velocity of this spectrum -- however, Domb's results (section 4d), and the numerical approximation made in chapter 7, appear to favour the velocity defined elastically through the adiabatic strain-energy $\mathcal{E}$.

4b: Initial Stresses.

The ordinary procedures and definitions of elasticity theory all refer to a medium which undergoes small deformations from an initial state of zero stresses. On the other hand, solid helium exists only under considerable pressure ($\sim$ 100

atmospheres at melting near $0^{\circ}K$) so that we are forced to consider any equivalent continuum as under initial stress, and to introduce the isotropic pressure (φ) into the thermodynamical discussion. It may be that the total strain from an imagined initial state+ of zero stresses could be regarded as small enough to allow the usual formulae to be applied to the total energy of deformation, total stresses, etc., but this is of no help, since the quantities of interest experimentally are the additional stresses and strain-energy, and even linear stress-strain relations are no longer expressible in the usual symmetrical form for these additional quantities; the usual results require the initial stresses to be negligible compared with the additional ones, which is not the case here.

As mentioned above, Huang (1950) has considered the definitions of elastic properties under initial stresses. It is clear that, parallel to the usual one, a theory concerning the additional displacements from a stressed equilibrium state can be set up, and the variational procedure used for obtaining equations of motion. The additional

+ Defined, say, by extrapolation, using the measured compressibility $\sim \frac{1}{10}$ per 100 atmos. for solid He.

strain-energy-density depends on the <u>total</u> stresses, and Huang has found that it cannot be expressed merely in terms of the symmetrical additional strain components $e_{\alpha\beta}$; he uses as variables the $u_{\alpha\beta}$ of a homogeneous deformation,

$$u_\alpha = \sum_\beta u_{\alpha\beta} x_\beta \,, \tag{4.3}$$

and writes

$$\Delta W = \sum_{\alpha\beta} S_{\alpha\beta} u_{\alpha\beta} + \frac{1}{2} \sum_{\alpha\beta} \sum_{\gamma\delta} S_{\alpha\beta,\gamma\delta} u_{\alpha\beta} u_{\gamma\delta} \,, \tag{4.4}$$

with

$$S_{\alpha\beta,\gamma\delta} = S_{\gamma\delta,\alpha\beta} \,, \tag{4.5}$$

from which by the variational procedure

$$\rho \ddot{u}_\alpha = \sum_\beta \left\{ \sum_{\gamma\lambda} S_{\alpha\gamma,\beta\lambda} \frac{\partial^2 u_\beta}{\partial x_\gamma \partial x_\lambda} \right\} , \tag{4.6}$$

homogeneous linear equations of motion arising since

$$0 = \sum_\beta \frac{\partial}{\partial x_\beta} S_{\alpha\beta} \,, \tag{4.7}$$

the expression of initial equilibrium[+]. The $S_{\alpha\beta}$ are thus the initial stresses, and these linear

+ When ΔW is reckoned from a lattice energy it is obtained per lattice cell, all cells being equivalent under a homogeneous deformation. The coefficients $S_{\alpha\beta}$, $S_{\alpha\gamma,\beta\lambda}$ are then constant lattice quantities, independent of position $\underline{x}$, and (4.7) again follows.

equations (4.6) can be used in correspondence with the linear adaptation method in the lattice theory.

By applying the postulate of rotational invariance to the energy (4.4) Huang derives the symmetry conditions

$$\left.\begin{aligned} \zeta_{\alpha\beta} &= \zeta_{\beta\alpha} \\ \zeta_{\alpha\delta}\,\delta_{\beta\gamma} + \zeta_{\alpha\beta,\gamma\delta} &= \zeta_{\beta\alpha,\gamma\delta} + \zeta_{\beta\delta}\,\delta_{\alpha\gamma} \end{aligned}\right\}; \tag{4.8}$$

the first of these is to be expected; the last differs from the usual

$$c_{\alpha\beta,\gamma\delta} = c_{\beta\alpha,\gamma\delta}, \tag{4.9}$$

the $c_{\ldots}$ being the ordinary elastic constants of the unstressed medium, and even in the case of isotropic pressure alone, $\zeta_{\alpha\beta} = \delta_{\alpha\beta}\zeta$, say, there remains one case in which (4.8) differs from (4.9):

$$\zeta_{\alpha\beta,\alpha\beta} = \zeta_{\beta\alpha,\alpha\beta} + \zeta, \quad \alpha \neq \beta. \tag{4.10}$$

Under (4.10) the energy (4.4) becomes

$$\Delta W = \sum_{\alpha\geq\beta} \zeta_{\alpha\beta} e_{\alpha\beta} + \tfrac{1}{2}\sum\sum_{\substack{\alpha\geq\beta \\ \gamma\geq\delta}} \zeta_{\alpha\beta,\gamma\delta}\, e_{\alpha\beta} e_{\gamma\delta} + \tfrac{1}{2}\zeta \sum_{\alpha\beta} u_{\alpha\beta}^2, \tag{4.11}$$

and this form must necessarily be used for solid helium. There is an apparent contradiction between such a formula and the symmetrical covariant formula introduced by Born (1942) on the basis of

a homogeneous deformation of the cell vectors $\underline{a}_\alpha$ of a lattice under possible stresses: this will be investigated elsewhere, since we will need to consider in detail only the trivial example of a linear chain. The strain energy (4.4) ought also to be invariant under any linear transformation $(xyz) \rightarrow (x'y'z')$ corresponding to a symmetry operation allowed by the lattice to which the continuum is equivalent. We will use the approximation of isotropy, for which the usual symmetry simplifications, as applied to the determination of the velocities of plane elastic waves quoted below, may be assumed to apply.

These velocities (c_j) are the three roots of the linear wave equations which follow immediately from (4.6):

$$\rho c^2 u_\alpha = \sum_\beta \left\{ \sum_{\gamma\lambda} S_{\alpha\gamma,\beta\lambda} \frac{\gamma_\gamma \gamma_\lambda}{\gamma^2} \right\} u_\beta \; ; \quad (4.12)$$

they obviously depend on the direction of the wave-vector (γ), but not in its magnitude (γ). Again, in general, the lattice symmetry must be considered in relation to these equations, but for the isotropic case we may continue to express the single velocity (c) by the usual formula (see, for example, Born (1923))

$$c = \sqrt[3]{\frac{3}{\chi(\sigma)}}\sqrt{\frac{1}{\rho\kappa}}\,, \qquad (4.13)$$

ρ being the density and κ, σ the compressibility and Poisson's ratio; $\chi(\sigma)$ is defined by

$$\chi(\sigma) = \left\{\frac{1+\sigma}{3(1-\sigma)}\right\}^{3/2} + 2\left\{\frac{2}{3}\,\frac{1+\sigma}{1-2\sigma}\right\}^{3/2}, \qquad (4.14)$$

and the evaluation of κ, σ must in the present application be made in the presence of a non-vanishing isotropic pressure p.

According to 4a, in making a comparison with lattice waves we should define the continuum in reference to its adiabatic wave motion so that κ, σ are to be derived from an additional strain energy function ΔW based on the internal energy $\mathcal{E}$. We then have

$$\left.\begin{aligned}\frac{1}{\kappa} &= -V\frac{\partial p}{\partial V} = V\frac{\partial^2 \mathcal{E}}{\partial V^2}\,,\\ p &= -\frac{\partial \mathcal{E}}{\partial V}\,;\end{aligned}\right\} \qquad (4.15)$$

where

for a cubic lattice of constant a, these become

$$\left.\begin{aligned}\frac{1}{\kappa} &= V\left\{\frac{\partial^2 \mathcal{E}}{\partial a^2} + p\,\frac{\partial^2 V}{\partial a^2}\right\}\Big/\left(\frac{\partial V}{\partial a}\right)^2,\\ p &= -\frac{\partial \mathcal{E}}{\partial a}\Big/\frac{\partial V}{\partial a}\,.\end{aligned}\right\} \qquad (4.16)$$

The density ρ is $\frac{M}{V}$, where M is the molar

mass, and $V = N\Delta$ [+]; thus the isotropic velocity is given by

$$c = \frac{\Delta}{\frac{d\Delta}{da}} \sqrt[3]{\frac{3}{f(\sigma)}} \sqrt{\frac{\frac{\partial^2 \xi}{\partial a^2} + Np \frac{\partial^2 \Delta}{\partial a^2}}{M}}, \qquad (4.17)$$

where the influence of the pressure is clearly shown.

The general question of elasticity under stresses will not be pursued further here, since in the Debye approximation which follows only the elastic velocities c_j, now known to exist as the roots of (4.12), will be required -- and in fact only the isotropic approximation to them.

4c: The Debye Approximation.

We need to apply the Debye approximation to the new lattice frequency distribution: to illustrate the effect of the non-linear theory, and of initial stresses, and to bring together all the relevant formulae, we will develop the well-known procedure briefly in this section.

[+] For the three types of cubic lattice we may write $\Delta = qa^3$;
with a defined (see chapter 6) as the nearest neighbour distance, q has the values

simple cubic	: 1
body-centred cubic	: $\frac{1}{2}$
face-centred cubic	: $\frac{1}{\sqrt{12}}$

The purpose of the approximation is to replace the complex spectrum of lattice frequencies by the simple distribution corresponding to the modes of vibration of an elastic medium. These can be represented by plane waves of wave normal $\underline{y}$ and velocities c_j $(j=1,2,3)$, functions of the direction of $\underline{y}$ but not of its magnitude; the remarks of 4b show that such waves and wave-velocities also exist under initial stresses, as in the helium case.

The permissible wave-vectors of a continuum are determined by the size and shape of the specimen and its boundary conditions. It is well known that for a large solid the actual boundary conditions have little effect on the distribution of possible modes of vibration, and that a cyclic condition will do instead. If a parallelopiped of edges $\underline{A}_1, \underline{A}_2, \underline{A}_3$ and volume $V=(\underline{A}_1 \wedge \underline{A}_2)\,\underline{A}_3$ contains a pattern of disturbances which is to be repeated on all sides, it is readily shown[+] that only those running waves are permitted for which $\underline{y}$ is some point of a "cyclic mesh" in the reciprocal $\underline{y}$-space defined by the vectors $\underline{B}_1 = \frac{\underline{A}_2 \wedge \underline{A}_3}{V}, \ldots$. The

+ In matrix notation, $\{y\}$ must be such that $Ay = p$, where the components of $\{p\}$ are any integers, and the $\{A_i\}$ are the columns of A. Then clearly $y = A^{-1}p$.

volume of a mesh cell is then $\frac{1}{V}$, so that V is the density of permitted wave-vectors; we suppose V to be large enough that to any element dW of the reciprocal space there correspond VdW such vectors. For each of the three velocities c_j the density of proper frequencies is then

$$dz_j = V\gamma^2 d\gamma\, d\Omega = \frac{V}{c_j^3} \nu_j^2 d\nu_j d\Omega , \tag{4.18}$$

where

$$\nu_j = c_j \gamma , \quad j = 1, 2, 3 , \tag{4.19}$$

γ being the modulus of $\underline{\gamma}$, and $d\Omega$ an elementary solid angle in the $\underline{\gamma}$-space. The relations (4.18), (4.19) extend to the whole of the elastic spectrum, the wave-number γ being as large as we please, and the assumption of the elementary density VdW enables sums over the proper frequencies to be replaced by integrals over the reciprocal space.

In practice the continuum is to correspond to an actual lattice having a unit cell of sides $\underline{a_1}$, $\underline{a_2}$, $\underline{a_3}$ and volume Δ, say, and the cyclic condition is to be applied to a block of, say, N cells so that $A_i = n\underline{a}_i$, $V = n^3\Delta = N\Delta$. If plane lattice waves can also be chosen to satisfy

the cyclic conditions their wave-vectors must be determined just as for the continuum above, except that now the periodicity of the medium implies that all distinct modal frequencies can be obtained by restricting $\underline{y}$ to one cell of the "reciprocal lattice", defined by the vectors $\underline{b}_1 = \frac{\underline{a}_2 \wedge \underline{a}_3}{\Delta}, \ldots$ or an equivalent region. There are clearly N cells of the cyclic mesh in each reciprocal lattice cell, and so N distinct permissible $\underline{y}$ -values corresponding to the volume V ; to each belong $3s$ frequencies when there are s atoms in the basis of the lattice, so accounting for the full $3Ns$ degrees of freedom of the N particles considered.

The possibility of obtaining cyclic plane waves as a solution of the lattice equations of motion is ordinarily shown by reference to their linear form and periodic coefficients, dependent on the quadratic terms in $\underline{\Phi}$ (e.g. Born (1923)). The partition properties of the lattice frequency distribution are also established in this way. For the non-linear helium solution we have <u>defined</u> in chapter 2 the transformation from the atomic coordinates (x) to the "normal" coordinates (q) in exactly the fashion which corresponds to solving the linear part of the equations of motion, using only the quadratic terms of $\underline{\Phi}$, and so exactly

the usual wave form for this transformation will still hold good. The only difference lies in the energy that is associated with the new coordinates -- the possibly negative ω^{o2} of the ordinary theory being replaced by positive ω^2, obtained by means of the adaptation method. Further, we can suppose an ω^2 to correspond to each ω^{o2}, so that the ω-distribution falls into the same branches as that of the usual ω^o. Lattice frequencies, cyclic conditions, and the Debye approximation, can thus be used for the new helium spectrum in the ordinary fashion.

Near the long-wave limit of the three acoustic branches of the lattice spectrum (they constitute the whole of it for a simple lattice, which is all that will be considered hereafter) we have the relations

$$\nu_i = c_i \chi \,, \quad i = 1, 2, 3 \,, \qquad (4.20)$$

similar to (4.19), with the c_i functions of the direction of $\underline{\chi}$ alone. The Debye approximation extends these relations to the whole of the acoustic branches, by analogy with (4.19), at the same time replacing sums over the proper frequencies by integrals (along each branch, that is to say).

This statement constitutes an (adiabatic) wave-definition of the equivalent continuum; more generally, we might define it from the energy density $\mathcal{E}$ according to the discussion of 4a, possibly with a different result in the helium case: which form of elastic definition is most useful in thermodynamical and other applications remains to be seen. Writing $\nu_j = c_j \gamma \; (j=1,2,3)$ for the whole acoustic spectrum, then, where the c_j are some suitable "elastic" velocities, we have

$$\underset{\text{acoustic frequencies}}{\sum \ldots} \longrightarrow \sum_{j=1}^{3} \int \nu \, dW \ldots$$

$$= \sum_{j=1}^{3} \int \nu \gamma^2 d\gamma \, d\Omega \ldots$$

$$= N\Delta \sum_{j=1}^{3} \int \nu_j^2 d\nu_j \, \frac{1}{c_j^3} \, d\Omega \ldots, \qquad (4.21)$$

the integrand being some function of ν. A well known procedure (e.g. Born, 1923) approximates the reciprocal lattice cell over which each $\int dW$ is to be taken by a sphere of radius $\sqrt[3]{\frac{3}{4\pi\Delta}}$, containing the same number of degrees of freedom, so that the three integrals run from $0 \rightarrow (\nu_D)_j$ where $(\nu_D)_j = c_j \sqrt[3]{\frac{3}{4\pi\Delta}}$. Any further simplification then depends on the spatial symmetry of the lattice under consideration.

The helium lattice is generally supposed to be of the close-packed hexagonal structure; for

thermodynamical purposes the close-packed cubic structure is a good approximation to this. The further approximation to isotropic symmetry does not make a great deal of difference in determining the elastic velocities c_j (for example, k, σ have the same form in terms of the elastic constants c_{11}, c_{12} for isotropy or for cubic symmetry); it provides a ready means of making the necessary calculations, and only the isotropic model will be considered hereafter. The velocities c_j are then independent of $\underline{\gamma}$ (or $d\Omega$). Defining an average velocity c and an average upper limit ν_D in the usual way (e.g. Born, 1923), we have Debye's form for (4.21),

$$\sum_{\substack{\text{acoustic} \\ \text{frequencies}}} \ldots \rightarrow 4\pi N\Delta \frac{3}{c^3} \int_0^{\nu_D} \nu^2 d\nu \ldots$$

$$= \frac{9N}{\nu_D^3} \int_0^{\nu_D} \nu^2 d\nu \ldots \qquad (4.22)$$

where

$$\nu_D = c \sqrt[3]{\frac{3}{4\pi\Delta}} , \qquad (4.23)$$

The upper limit is usually written in terms of the characteristic temperature Θ_D defined by

$$\Theta_D = \frac{h}{k} \nu_D \; ; \qquad (4.24)$$

this will appear in the next section as "the constant Debye parameter" characteristic of a given substance. The Debye frequency, ν_D, is of course of the same order as the maximum lattice frequency, ν_m.

It remains to fix the velocities c_j which appear as the parameters in the general Debye approximation (or the $(\nu_D)_j$, or $(\theta_D)_j$ which are equivalent to them) -- as mentioned above, this is the problem of defining a continuum atomistically, in the form relevant to a thermodynamical discussion. For the most used isotropic case, the single average velocity c (or ν_D, or θ_D) must be determined; in the following we shall approximate to it by using the velocity of elastic waves in the linear chain as considered in the next chapter: this appears to give reasonable numerical results in the helium application.

4d: Discussion of Domb's Formula for θ.

The specific heat at constant volume is given in Debye's isotropic approximation by the formula

$$C\left(\frac{\theta_D}{T}\right) = 3R\left\{4D\left(\frac{\theta_D}{T}\right) - 3P\left(\frac{\theta_D}{T}\right)\right\}, \quad (4.25)$$

where $D(x)$ is Debye's function

and $P(x)$ is Planck's function, defined in chapter 3. It is well known that the discrepancy between the Debye spectrum and the actual lattice spectrum is in most cases reflected by the failure of this formula over a range of temperature at any one volume, Θ_D being kept fixed according to its definition in the previous section, and it has become customary to define a variable Debye parameter, Θ_T, chosen so as to restore the agreement between (4.25) and the experimental results. The variation of Θ_T with T at constant volume does not, of course, represent any real variation in the elastic properties of the lattice; when these are exactly defined through $\mathcal{E}$ or $\mathcal{F}$, rather than Φ, there will be such a variation, and Θ_D will vary accordingly, but this is a very slight effect and quite distinct from the empirical changes in Θ_T. In practice, even the latter are relatively small, being only some 10% of the value of Θ, and in the case of solid helium this is not of much account compared to the possible change in Θ with volume, say along the melting curve. It will be found in Chapter 7 that our non-linear theory can allow, at each volume, an average value of Θ_T to be chosen -- though not by the formula (4.25) -- which gives a close estimate of specific

heats over practically the whole possible range of temperature and is in reasonable agreement with elastic theory: the distinction between the various values of Θ_T and Θ_D is then not of very great importance.

Domb and Salter (1952) have set up a formula for the empirical Θ_T in the case of an ordinary face-centred cubic lattice by comparing an expression for the specific heat (due to Thirring, (1913,14)) in terms of the even moments of the lattice spectrum with that in terms of the moments of an isotropic Debye spectrum by a perturbation method, assuming the quantity $\frac{h\nu_m}{kT}$ to be small. They obtain

$$\Theta_T = \frac{h}{k}\sqrt{\frac{5\mu_2}{3}}\left\{1 - \frac{21I_4 - 25I_2^2}{840I_2}\left(\frac{h\nu_m}{kT}\right)^2 + \cdots\right\}, \qquad (4.26)$$

where $I_{2n} = \frac{\mu_{2n}}{\nu_m^{2n}}$. For the lattice in question they evaluate μ_{2n} from the matrix of coefficients in the usual linear equations of motion of the atoms, using assumed force constants and next neighbour interactions (not an essential restriction), thus expressing everything in terms of Φ [+]; in particular, it follows that

$$\mu_2 = \frac{1}{\pi^2}\frac{\Phi''(a)}{M}, \qquad (4.27)$$

+ The derivatives of Φ refer, of course, to the reference configuration.

where again M is the molar mass, a the cubic lattice constant, and $'$ denotes $\frac{d}{da}$. They also calculate the zero-point energy ε_0 from the first odd moment of the spectrum and find that the equation

$$\varepsilon_0 = \frac{9}{8} R \frac{h}{k} \sqrt{\frac{5\mu_2}{3}} \qquad (4.28)$$

is well satisfied.

The essential part of these formulae is the relation

$$\omega_\infty = \frac{h}{k}\sqrt{\frac{5\mu_2}{3}} = \left(\frac{1}{\pi}\sqrt{\frac{5}{3}}\right)\frac{h}{k}\sqrt{\frac{\Phi''(a)}{M}}\,, \qquad (4.29)$$

in Domb's notation, and this is exactly proportional to the usual elastic definition of ω_D considered in the preceding section: (4.23), (4.24), together with the relations for the isotropic velocity c given in 4b, imply

$$\omega_D = \frac{\Delta}{\frac{d\Delta}{da}}\sqrt[3]{\frac{9}{4\pi\Delta\chi(\sigma)}}\cdot\frac{h}{k}\sqrt{\frac{\Phi''(a)}{M}}\,, \qquad (4.30)$$

when it is remembered that the discussion here concerns an ordinary unstressed lattice ($p=0$) with its elastic properties based on Φ -- i.e., such that the vibrational part of the energy ε, in

$$\mathcal{E} = \Phi + \mathcal{E}_0 + \mathcal{E}_T$$

can be neglected. Since Δ is proportional to a^3 the factors in Δ are independent of a; we may also assume the factor $\chi(\sigma)$ to be practically constant: the behaviour of Θ_D is then governed by the quantity $\sqrt{\Phi''(a)/M}$ in the same way as that of Θ_∞. The formula (4.28) for the zero-point energy, in terms of the limiting value of Θ_T, is thus equivalent to the Debye formula

$$\mathcal{E}_0 = \frac{9}{8} R \Theta_D , \qquad (4.31)$$

derived from the (constant) one-parameter theory, and may be expected to show the right variation with volume; absolute values may depend on the adjustment of numerical constants and are not of much importance.

A more interesting case of relative variation with volume is that of solid helium, and in a further paper Domb (1952) has remarked that formulae based on $\sqrt{\Phi''(a)/M}$ may then break down completely, since at molar volumes ~ 15 cc or more (see chapter 6) $\Phi''(a)$ becomes negative. He proposes to use a quantity like the Θ_∞ above, but with Φ replaced by $\Phi + \mathcal{E}_0$ -- just the procedure discussed in 4a to take account of a

relatively large zero energy. The definition (4.29) of the limiting Θ_T then becomes

$$\Theta_0 = \left(\frac{1}{\pi}\sqrt{\frac{5}{3}}\right)\frac{h}{k}\sqrt{\frac{\Phi_L''(a) + \mathcal{E}_0''(a)}{M}}, \quad (4.32)$$

and Domb has found that this result can be used successfully well beyond the volume mentioned above.

It is obvious that the success of this formula lies in the fact that it is an approximate definition of the elastic Θ_D which can be defined for solid helium, when we bear in mind the fact that the differences between the various empirical Θ_T's and Θ_D is of no importance compared, in this case in particular, with their common dependence on volume. Using the full adiabatic formulae[+] for the average velocity c quoted above we would have

$$\Theta_D = \frac{\Delta}{\frac{d\Delta}{da}}\sqrt[3]{\frac{9}{4\pi\Delta\chi(\sigma)}}\cdot\frac{h}{k}\sqrt{\frac{\frac{\partial^2\mathcal{E}}{\partial a^2} + N_p\frac{\partial^2\Delta}{\partial a^2}}{M}}; \quad (4.33)$$

Domb's formula omits the $\chi(\sigma)$ term, the pressure term, and the thermal term $\frac{\partial^2\mathcal{E}_T}{\partial a^2}$. These omissions are not, in fact, very important: the first has been mentioned above, and is anyway unavoidable

+ The alternative choice of the limiting lattice velocity may, in fact, give much the same volume-dependence for Θ; in any case the new frequencies lie outside the scope of Domb's work.

for solid helium, where the elastic constants are not known, and the pressure term and the thermal term together can be shown to give corrections of only some 10% compared with $(\Phi + \varepsilon_0)''$.

It is equally clear that the method of deriving (4.29) as a limiting case of the Θ_T got by the perturbation procedure (4.26) can no longer be used to obtain (4.32), and it would be better not to regard the latter as a limiting Θ_T at all: rather, with a suitable choice of numerical factors, it is the elastically defined Θ_D of (4.33) itself. The melting temperature of solid helium at the experimental molar volumes considered in chapter 7 is $\sim 10^\circ K$, whereas $\frac{h\nu_m}{k} \sim 100^\circ K$; $\frac{h\nu_m}{kT}$ is then not a small fraction, and the perturbation procedure will not converge satisfactorily. Moreover, the (absolute) moments of the frequency spectrum μ_r, which depend on the actual values of the lattice frequencies $\omega(\vec{k}_j)^2$, are no longer given by the matrix of quadratic terms (which determines $\omega(\vec{k}_j)^{0\,2}$) in the now non-linear equations of motion, and the usual force constants are not sufficient (nor are any known for helium); nor can any numerical confirmation of (4.28) now be made from the ordinary formulae for

μ_1 and μ_2. As mentioned above, although an empirical Θ_T can still be calculated directly from (4.25) and the experimental specific heats, it is not the relevant Θ_T which our non-linear theory would propose to account for these experiments and which has an absolute connection with the elastic Θ_D appropriate to that theory: this difference is to be seen in the formulae of chapter 3, and is made plain numerically in chapter 7; it also follows from the non-linear theory that the expression for ε_0 differs somewhat from the usual (4.28) and we may write, by (3.21),

$$\varepsilon_0 = \left\{ \frac{3+f(a)}{4} \right\} \frac{9}{8} R \Theta_D . \qquad (4.34)$$

In practice, for the threedimensional helium lattice, the zero energy ε_0 is not known, and Domb has approximated the term $\varepsilon_{0(a)}''$ by the Debye expression $\frac{9}{8} R \Theta_{D(a)}''$, based on (4.28); in the elastic formula (4.33) we should have to do the same, except that now the volume dependence of the factor $\left\{ (3+f(a))/4 \right\}$ in (4.34) ought to be taken into account -- however, it is to be expected that the expression $\left\{ (3+f(a))/4 \right\} \frac{9}{8} R \Theta_{D(a)}''$ will account for the main part of $\varepsilon_{0(a)}''$. The result of this $\Theta_{(a)}''$ approximation is to turn (4.32) or (4.33)

into a differential equation in ω ,

$$\Theta = \text{const.} \frac{h}{k} \sqrt{\frac{\Phi''(a) + \text{const.} \frac{9}{8} R \Theta''(a)}{M}} , \quad (4.35)$$

a relation which must be approximately satisfied if the Debye theory is to be used consistently in various thermodynamical functions. Domb has taken the values of Θ_T calculated along the melting curve from recent specific heat measurements of Dugdale and Simon (—) by the formula (4.25), derived values of $\Theta_T''(a)$ from them, and shown that these quantities can be made to satisfy (4.35) fairly closely over the whole range of molar volume from $\sim$ 10 cc to 20 cc; some numerical considerations of (4.35) will also be made in chapter 7.

If the zero energy could be worked out independently, or if $\Theta_D''(a)$ were known separately -- say from the variation of Gruneisen's expansion coefficient+ γ , then (4.35) could properly be

+ This is defined as

$$\gamma = -\frac{V}{\Theta_D}\frac{d\Theta_D}{dV} = -\frac{1}{3}\frac{a}{\Theta_D}\Theta_D'(a) ,$$

the latter for a cubic lattice. In the usual theory it is connected with the coefficient of volume expansion α by the formula

$$\gamma = \alpha V / \kappa C ;$$

in the present case in which the vibrations are essentially non-linear this connection should be investigated further. It has in fact been verified empirically by Dugdale (1951), and can also be shown empirically according to our non-linear theory -- see chapter 7.

used as an equation to determine Θ_D. In chapter 7 we will estimate Θ_D differently, by approximating to the isotropic velocity c in the definitions (4·23) and (4·24) by the velocity in the linear chain (see chapters 5 and 6).

Domb's approximation to ε_0'' in (4·35) obscures the necessity for a new definition of lattice frequencies in the helium case, though this necessity is of course implied by his consideration of the lattice beyond the inflexion point $\Phi''(a) = 0$. Indeed, so long as ε_0 itself does not have to be worked out there need not be any vibrational motion at all (e.g. the free-particle model of London (1936) could be used); an empirical Debye approximation could always be set up. The non-linear theory shows that there is no need to discard the vibrational picture and provides exact expressions for the constants and parameters involved in the preceding discussion.

CHAPTER 5 : THE LINEAR CHAIN.

5a: The Potential Function in the Linear Chain.

In the following sections we will consider the example of a linear, monatomic chain[+] such as was studied by Born and Von Kármán (1912).

The atoms will be assumed to interact with central forces, and potential

$$\phi_{ll'} = \phi(|x_l - x_{l'}|) , \qquad (5.1)$$

where x_l is the coordinate of the l-th atom measured along the chain. Usually we will consider only next neighbour (n/n) interactions, the extension to all neighbours being on the whole obvious; the chain potential in the general case would be

$$\mathcal{U} = \tfrac{1}{2} \sum_{ll'}{}' \phi_{ll'} , \qquad (5.2)$$

and under the n/n restriction,

$$\mathcal{U} = \tfrac{1}{2} \sum_{l,l'=l\pm1} \phi_{ll'} . \qquad (5.3)$$

+ There is no need to consider a polyatomic linear chain, as we will not consider the analogous three-dimensional lattice with a basis in any detail, the helium lattice being taken as a cubic Bravais lattice of the face-centered type; the formulae for the polyatomic chain could be written down without much difficulty.

The chain may be finite, in which case end effects will appear, the atoms being slightly further apart (in their reference positions) at the ends; or it may be infinite, and normalised to a finite length according to the cyclic boundary condition (see Chapter 4). The latter model has been fully discussed elsewhere (Born 1942a, Brillouin 1946, etc.), with particular reference to its spectrum of proper frequencies, and will be used on most occasions; in it, all positions of reference are equally spaced.

We will consider either (a) a cyclic chain with its period covering n atoms or (b) a finite chain of n atoms (free ends), and n/n interactions. The indices l, l' will be restricted to the numbers $1 \ldots n$ in this way:

(a) $$\mathcal{U} = \frac{1}{2} \sum_{ll'=l\pm1}^{(n)} \phi_{ll'} , \qquad (5.4)$$

where terms with $l'=0, n+1$ are written as for $l'=n, 1$;

(b) $$\mathcal{U} = \frac{1}{2} \sum_{l,l'=l\pm1}^{(n)\,\prime\prime} \phi_{ll'} , \qquad (5.5)$$

where the $''$ means omitting terms with $l'=0, n+1$. The various derivatives of $\mathcal{U}$ with respect to the x_l follow immediately:

$$u_\ell = -\phi'_{\ell+1,\ell} + \phi'_{\ell,\ell-1} ,$$

$$u_{\ell\ell'} = -\delta_{\ell+1,\ell'}\phi''_{\ell+1,\ell} - \delta_{\ell-1,\ell'}\phi''_{\ell,\ell-1} + \delta_{\ell\ell'}\left(\phi''_{\ell+1,\ell} + \phi''_{\ell,\ell-1}\right),$$

$$u_{\ell\ell'\ell''} = \delta_{\ell\ell'}\left[\delta_{\ell\ell''}\left(\phi'''_{\ell,\ell-1} - \phi'''_{\ell+1,\ell}\right) + \delta_{\ell-1,\ell''}\phi'''_{\ell,\ell-1} - \delta_{\ell+1,\ell''}\phi'''_{\ell+1,\ell}\right], \qquad (5.6)$$

$$u_{\ell\ell'\ell''\ell'''} = \delta_{\ell\ell'}\left\{\delta_{\ell'\ell''}\left[\delta_{\ell''\ell'''}\left(\phi^{IV}_{\ell+1,\ell} + \phi^{IV}_{\ell,\ell-1}\right) - \delta_{\ell''+1,\ell'''}\phi^{IV}_{\ell+1,\ell} - \delta_{\ell''-1,\ell'''}\phi^{IV}_{\ell,\ell-1}\right]\right.$$
$$\left. + \delta_{\ell''\ell'''}\left[\delta_{\ell'-1,\ell''}\phi^{IV}_{\ell,\ell-1} + \delta_{\ell'+1,\ell''}\phi^{IV}_{\ell+1,\ell}\right]\right\},$$

where the convention is made of writing equal suffixes first in the $u_{\ell\ell'\ldots}$ (in lattice sums the terms must be grouped properly); it is clear that no more than two suffixes can be involved in any one term, and that the sign is + or − according as the second suffix appears an even or odd number of times; the arguments of the terms are the various $|x_\ell - x_{\ell'}|$ <u>in the reference spacing</u> of the general theory. Clearly, these formulae can immediately be extended to interactions over second, ... neighbours by writing $u = \frac{1}{2}\sum_r \sum_{\ell,\ell'=\ell\pm r} \phi_{\ell\ell'}$, $u_\ell = -\sum_r \phi'_{\ell+r,\ell} + \sum_r \phi'_{\ell,\ell-r}$, and so on.

The matrix $[e^0_{\ell m}]$ has been defined in 2b as that which transforms the quadratic terms of u into diagonal representation, with latent

roots $\omega_n^{o\,2}$+; these $\{e^o_{\ell n}\}$ and $\omega_n^{o\,2}$ satisfy the secular equations

$$\sum_{\ell} u_{\ell\ell'} e^o_{\ell n} e^o_{\ell' n'} = m\omega_n^{o\,2}\,\delta_{nn'} \qquad (5.7)$$

m being the common atomic mass. If the reference spacing is regular, say

$$x_\ell - x_{\ell'} = (\ell - \ell')a, \qquad (5.8)$$

the $e^o_{\ell n}$ and $\omega_n^{o\,2}$ are well-known; whenever an infinite (cyclic, regular) lattice solution of the general theory is proposed only such a regular solution of the secular equations (5.7) is required, and the same is true under the perturbation solution of the finite, non-regular case, since the $e^o_{\ell n}$, ω^o_n appear only in correction terms then; any more general solution of a non-regular case will not be considered in this work.

Under (5.8), the matrix $u_{\ell\ell'}$ for n/n interactions follows directly from (5.6), in the case (a)++, as

+ It is convenient to write the V_{nn} as $\omega_n^{o\,2}$ here, even though at the volumes considered for solid helium they may become negative; for ordinary substances and for small helium molar volumes, $\omega_n^{o\,2}$ is positive and frequencies ω_n^o exist; for large helium molar volumes, real ω_n^o do not exist - and this is of course the reason for having a new theory.

++ We could write Φ here instead of u, parallel to the general lattice case, but it will be more convenient to retain the general notation in this working, as mentioned above.

$$\left[u_{ll'}\right] = \begin{bmatrix} 2 & -1 & & & -1 \\ -1 & 2 & -1 & & \\ & \ddots & \ddots & \ddots & \\ & & -1 & 2 & -1 \\ -1 & & & -1 & 2 \end{bmatrix} \phi''(a), \tag{5.9}$$

with e^{0}_{lm} (real), and $\omega_m^{0\,2}$, given by

$$\omega_m^{0\,2} = \omega_m^{0\,2} \sin^2\left(\tfrac{1}{2}\psi_h\right), \quad h = 0 \ldots n-1,$$

$$e^{0}_{lm} = \begin{cases} \sqrt{\frac{1}{n}} \cos l\psi_h, & h = 0, \frac{n}{2} \\ \sqrt{\frac{2}{n}} \cos l\psi_h, & h = 1 \ldots \frac{n}{2}-1 \\ \sqrt{\frac{2}{n}} \sin l\psi_h, & h = \frac{n}{2}+1 \ldots n-1 \end{cases} \tag{5.10}$$

(we may take n even), where the maximum frequency is

$$\omega_m^{0} = 2\sqrt{\frac{\phi''(a)}{m}},$$

which may or may not be real (see footnote above), and

$$\psi_h = h\,\frac{2\pi}{n}.$$

Each frequency appears twice (in general), the corresponding vectors $\{e^{0}_{lm}\}$ (h fixed) representing (for positive $\omega_m^{0\,2}$) two standing waves with constant phase relation and the same amplitude, and we may combine them to form two independent, opposite running waves of the same frequency (the

exceptions $k=0$, $\frac{n}{2}$ are obviously trivial); the wave numbers cover the reciprocal k-axis uniformly at intervals of $\frac{2\pi}{n}$ in the range $0 \longrightarrow \pi$, counting doubly, or $0 \longrightarrow 2\pi$, counting singly and in analogy with the general cyclic case (see Chapter 4, and Fig. 5.1).

In the case (b), supposing regularity to the ends, as in (5.8),

$$\{u_{ll'}\} = \begin{bmatrix} 1 & -1 & & & \\ -1 & 2 & -1 & & \\ & \ddots & \ddots & \ddots & \\ & & -1 & 2 & -1 \\ & & & -1 & 1 \end{bmatrix} \phi''(a) , \qquad (5.11)$$

with real e^0_{ln} , and ω^0_n , given by

$$\omega_n^{0\,2} = \omega_m^{0\,2} \sin^2\left(\tfrac{1}{2}\psi_n\right) , \; k=0 \ldots n-1,$$

$$e^0_{ln} = \sqrt{\frac{1}{n}} , \; k=0 , \qquad (5.12)$$

$$\sqrt{\frac{2}{n}} \cos\left(k-\tfrac{1}{2}\right)\psi_n , \; k=1 \ldots n-1,$$

where the maximum frequency is again

$$\omega^0_m = 2\sqrt{\frac{\phi''(a)}{m}}$$

(which again may become imaginary as above), and

$$\psi_n = k\frac{\pi}{n} .$$

Each vector $\{e^0_{ln}\}$ (k fixed) represents (positive $\omega^{0\,2}_n$) a standing wave, or can be imagined as the

superposition of two non-independent opposite running waves; the wave-numbers h cover the reciprocal h-axis uniformly at intervals of $\frac{\pi}{n}$ in (say) the range $0 \rightarrow \pi$ (see Fig. 5.1), there being n separate frequencies.

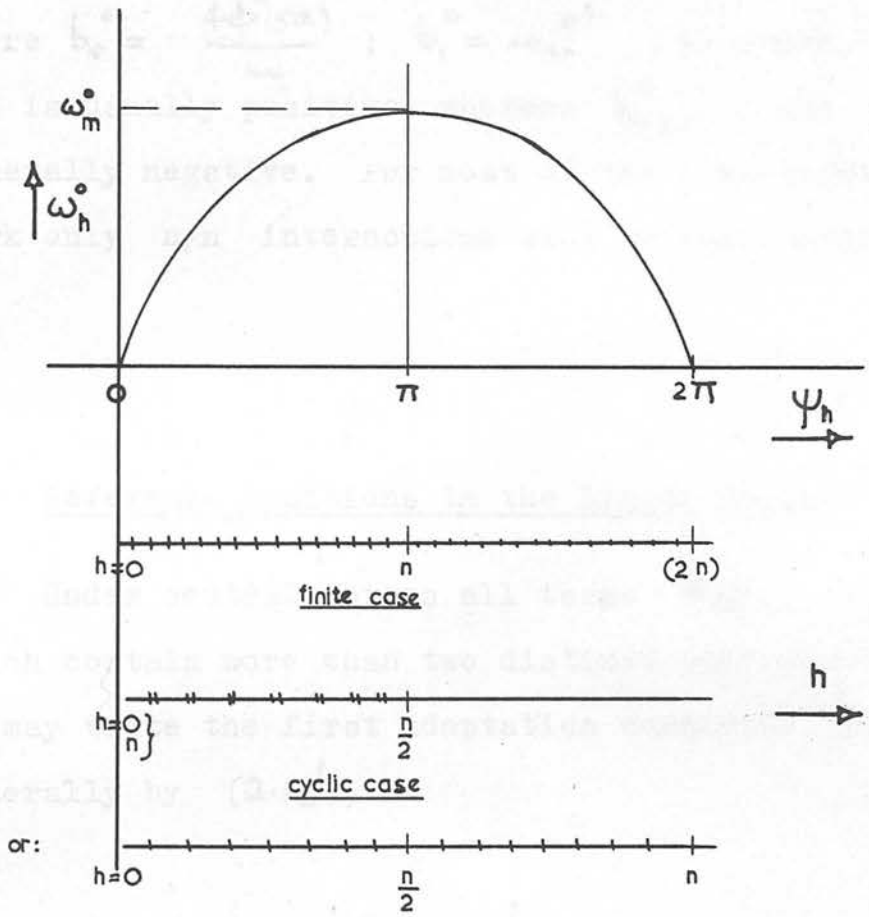


Fig. 5.1 : Frequency distribution in linear chain.

The generalisations of (5.9–12) for second.... neighbour interactions could readily be made, and are well-known to give formulae for the frequencies of the form

$$\omega_n^{o2} = \sum_r b_r^o \sin^2\left(\tfrac{1}{2}r\psi_n\right), \qquad (5.13)$$

where $b_r^o = \dfrac{4\phi''(ra)}{m}$; $b_1^o = \omega_m^{o2}$ as above, and is usually positive, whereas $b_2^o, \ldots$ are generally negative. For most of the subsequent work only n/n interactions will be considered.

5b: Reference Positions in the Linear Chain.

Under central forces all terms $u_{ll'}\ldots$ vanish which contain more than two distinct suffixes, and we may write the first adaptation condition, given generally by (2.13'), as

$$-u_l = \frac{1}{m}\sum_n \lambda_n \left\{ u_{ll} e_{ln}^2 + 2\sum_{l'}{}' u_{ll'} e_{ln} e_{l'n} + \sum_{l'}{}' u_{ll'} e_{l'n}^2 \right\}. \qquad (5.14)$$

For n/n interactions in the linear chain we have, by (5.6),

$$\phi'_{l+s,l} - \phi'_{l,l-1} = \frac{1}{m}\sum_n \lambda_n \left\{ (e_{l+n} - e_{l-1+n})^2 \phi'''_{l,l-1} - (e_{l+s+n} - e_{l+n})^2 \phi'''_{l+s,l} \right\}, \tag{5.15}$$

where $l = 1 \ldots n$, with the omission of some terms in the finite case (b); we may also write this as[+]

$$\phi'_{l+s,l} + \left\{ \frac{1}{m}\sum_n \lambda_n (e_{l+s+n} - e_{l+n})^2 \right\} \phi'''_{l+s,l}$$

$$= \phi'_{l,l-1} + \left\{ \frac{1}{m}\sum_n \lambda_n (e_{l+n} - e_{l-1+n})^2 \right\} \phi'''_{l,l-1} \quad * \tag{5.15'}$$

for $l = 1 \ldots n$ in the cyclic case, and in addition

$$= 0 \tag{5.15''}$$

for the finite case, from the end-equations.

We will propose as a non-linear[++] solution of the cyclic chain the regular spacing (5.8), so that

+ The extension of these formulae to further neighbour interactions can immediately be made by writing $l \pm r$ for $l \pm 1$ throughout and introducing an extra sum, $\sum_r$, for a suitable range of values of r, $r = 1, 2, 3 \ldots$. The solution corresponding to a regular cyclic chain then proceeds just as below, with a result analogous to (5.16), and the adaptation condition becomes an identity. For the finite case, the solution is more complicated, since at the ends the interactions become progressively more and more unbalanced; the result, however, is essentially similar to that given.

++ See discussion of (2b).

$$\left.\begin{aligned}\phi'_{\mu,\ell} &= \phi'(a)\\ \phi''_{\mu,\ell} &= \phi''(a)\end{aligned}\right\},$$

independent of ℓ. According to the general procedure for the non-linear solution the $e_{\mu\nu}$ are to be chosen as the $e^0_{\mu\nu}$, which in this regular case have the values given in (5.10). We find in

(5.15)

$$\frac{1}{m}\sum_{\nu}^{(m)}\lambda_\nu\left(e^0_{\mu,\mu+\nu}-e^0_{\ell,\nu}\right)^2=\frac{1}{m}\sum_{\nu}^{(\frac{m}{2})}\lambda_\nu\left\{\left(e^0_{\mu,\mu+\nu}-e^0_{\mu\nu}\right)^2+\left(e^0_{\mu,\mu+m-\nu}-e^0_{\ell,m-\nu}\right)^2\right\}$$

$$=\frac{8}{mm}\sum_{\nu}^{(\frac{m}{2})}\lambda_\nu\sin^2\left(\tfrac{1}{2}\psi_\nu\right);$$

(5.16)

in deriving this result we need a property of the ω_ν^2 (these being the non-linear solutions of the second adaptation condition) analogous to that of the ω_ν^{02} above by which $\omega_\nu^0=\omega_{m-\nu}^0$, so that $2\lambda_\nu=\bar{q}_\nu^2=\frac{k}{2\omega_\nu}\coth\left(\frac{1}{2}k\omega_\nu/kT\right)=\bar{q}_{m-\nu}^2=2\lambda_{m-\nu}$: it will be seen in 5c that the regular-chain solutions of the ω_ν^2 have this property. The expression (5.16) is independent of ℓ, so that (5.15') is identically satisfied,

$$\phi'(a)+\frac{8\phi''(a)}{mm}\sum_{\nu}^{(\frac{m}{2})}\lambda_\nu\sin^2\left(\tfrac{1}{2}\psi_\nu\right)=\text{constant};$$

(5.17)

the first adaptation condition thus leads to nothing

when a regular chain is proposed as a solution, and such a solution is possible; the spacing of the chain (a) must be got from thermodynamical considerations, using the free energy $\mathcal{F}$, and this will be done later.

As an example of the perturbation method of solution[+] we will consider the finite chain (case (b) above), supposing third and fourth degree terms in u to be small. The zero-order solution of (5·15″) is

$$\phi'_{m,l} = \phi'_{l,m} = \cdots = 0, \qquad (5\cdot18)$$

so that the reference spacing is then $x^\circ_{l+1} - x^\circ_l = \cdots = a^\circ$, say, corresponding to the minimum position of the potential ϕ. In the third-degree correction term of (5·15″) must appear the zero order solutions of the e_m, ω_n (see the perturbation procedure in 5c) which are, in fact, the e°_m, ω°_n; they are to be taken for the regular spacing of (5·18), since the perturbation procedure proceeds for the two adaptation conditions simultaneously, and so are given by (5·12), with a° written for a. Putting these various quantities into the right-hand-side of (5·15), we have

+ See discussion of 2b.

$$\frac{1}{nn}\sum_{n}\chi_n\left(e_{\ell+n,n}-e_{\ell,n}\right)^2=\frac{8}{nnn}\sum_{n}\chi_n^{(0)}\sin^2\left(\tfrac{1}{2}\psi_n\right)\sin^2\left(\ell\psi_n\right),$$

$$\chi_n^{(0)}=\tfrac{1}{2}\overline{q}_n^2(a^0,\omega_n^0), \qquad (5.19)$$

which remains dependent on ℓ ; thus the first order solution of (5.15'') is

$$a^1_{\ell+n,\ell}\equiv x^{\ell+n}_{2\ell+1}-x^{\ell+n}_{\ell}=-\frac{\phi'''(a^0)}{\phi''(a^0)}\frac{8}{nnn}\sum_{n}\chi_n^{(0)}\sin^2\left(\tfrac{1}{2}\psi_n\right)\sin^2\left(\ell\psi_n\right), \qquad (5.20)$$

which is positive (from the shape of the usual $\phi(a)$ curve).

The solutions (5.18), (5.20) illustrate the difference outlined in the introduction between this adaptation approach and earlier theories: (5.18) fixes the x_ℓ^{eq} in those minimum positions hitherto used in defining a lattice, while (5.20), arising from the third degree terms of $\mathcal{U}$, takes account of thermal expansion (through the $\chi_n=\tfrac{1}{2}\overline{q}_n^2$) as well as expressing the finite boundary effects. We can simplify (5.20) under the assumption that the temperature is small by writing $2\chi_n=\overline{q}_n^2\sim\frac{t}{2\omega_n}$, so that

$$a^1_{\ell+n,\ell}\sim-\frac{\phi'''(a^0)}{\phi''(a^0)}\frac{t}{n\sqrt{n\phi''(a^0)}}\frac{1}{4}\cot\frac{\pi}{4n}\left\{1-\frac{\sin^2\frac{\pi}{4n}}{\sin^2\frac{\ell\pi}{n}}\right\}^{-1}$$

$$\sim-\frac{\phi'''(a^0)}{\phi''(a^0)}\frac{t}{\sqrt{n\phi''(a^0)}}\frac{16\ell^2}{\pi(16\ell^2-1)}, \qquad (5.20')$$

for large n ; the effect of the last factor is slight, the ratios of successive spacings from either end to that in the interior being as 1·05 : 1·01 : 1·0001 : ..... , so that there is negligible inaccuracy in replacing the finite boundaries by the regular, cyclic condition; this will remain fairly true at higher temperatures -- the more so the smaller the thermal effects are in comparison with zero vibrations (always subject to the conditions of the perturbation solution, of course). The interior spacing is given by

$$a^{I} \sim -\frac{\phi'''(a^0)}{\phi''(a^0)} \frac{\hbar}{\pi\sqrt{m\,\phi''(a^0)}} , \qquad (5\cdot20'')$$

which will be found below to agree with the perturbation solution of the minimum free energy condition proposed above to define a in the cyclic case, again confirming this cyclic approximation.

5c: Vibrations in the Linear Chain.

Again, under central forces, we may write the various $u_{ll'...}$ in terms of two indices, and the second adaptation condition, given generally by

(2·13′), becomes

$$m\omega_n^2 \delta_{nn'} = \sum_{ll'} u_{ll'} \tfrac{1}{2}(e_{ln}e_{l'n'} + e_{ln'}e_{l'n}) +$$

$$+\Bigg[\sum_{ll'} u_{lll'l'} A_{ll'} e_{ln}e_{ln'} + \sum_{ll'}{}' u_{llll'}\left(2A_{ll'} e_{ln}e_{ln'} + A_{ll}\{e_{ln}e_{l'n'} + e_{ln'}e_{l'n}\}\right)$$

$$+\sum_{ll'}{}' u_{lll'l'} A_{ll'}\left(e_{ln}e_{l'n'} + e_{ln'}e_{l'n}\right)\Bigg], \tag{5·21}$$

where $A_{ll'}$ is given by (2·17). For n/n interactions in the linear chain we have, by (5·6),

$$m\omega_n^2 \delta_{nn'} = \sum_{t=\pm} \sum_{l} \phi''_{l\pm1,l}\left\{e_{ln}e_{ln'} - \tfrac{1}{2}\left(e_{ln}e_{l\pm1,n'} + e_{ln'}e_{l\pm1,n}\right)\right\} +$$

$$+\sum_{t=\pm} \sum_{l} \phi^{iv}_{l\pm1,l}\left\{\left(A_{ll} + A_{l\pm1,l\pm1} - 2A_{l,l\pm1}\right)e_{ln}e_{ln'}\right.$$

$$\left.+\left(A_{l,l\pm1} - A_{ll}\right)\left(e_{ln}e_{l\pm1,n'} + e_{ln'}e_{l\pm1,n}\right)\right\}, \tag{5·22}$$

where the sign $\sum_{t=\pm}$ means adding the following terms taken firstly with $l+1$ throughout, secondly with $l-1$ throughout, and $l=1,\ldots,n$, with the omission of some terms in the finite case (b)+.

+ The extension to more distant interactions is again made simply by inserting an extra summation, $\sum_{r}$, and writing $l\pm r$ in place of $l\pm1$.

We again propose as a non-linear solution of the cyclic chain the regular spacing (5.8), so that

$$\left.\begin{aligned}\phi''_{\ell n,\ell} &= \phi''_{(a)}\\ \phi^{IV}_{\ell n,\ell} &= \phi^{IV}_{(a)}\end{aligned}\right\},$$

independent of ℓ. The $e_{\ell n}$ once more are to be chosen as the $e^0_{\ell n}$, with the values of (5.10), this being the regular case (a), and the non-diagonal equations ($h \neq h'$) in (5.22) drop out of consideration[+]. The diagonal equations now become

$$m\omega_n^2 = 2\phi''_{(a)} \sum_\ell \left\{ e^{o\,2}_{\ell n} - \frac{1}{2} \sum_{+,-} e^0_{\ell n} e^0_{\ell\pm 1, n} \right\} +$$

$$+\phi^{IV}_{(a)} \sum_\ell \left\{ 2A_{\ell\ell} e^{o\,2}_{\ell n} + \sum_{+,-} \left(A_{\ell\pm 1,\ell\pm 1} - 2A_{\ell,\ell\pm 1}\right) e^{o\,2}_{\ell n} \right.$$

$$\left. +2 \sum_{+,-} \left(A_{\ell,\ell\pm 1} - A_{\ell\ell}\right) e^0_{\ell n} e^0_{\ell\pm 1, n} \right\}. \quad (5.23)$$

The known values of the $e^0_{\ell n}$ from (5.10) lead directly to the results

+ These non-diagonal equations are now

$$0 = \sum_{+,-} \sum_\ell \left\{ e_{\ell n} e_{\ell n'} - \tfrac{1}{2}\left(e_{\ell n} e_{\ell\pm 1, n'} + e_{\ell n'} e_{\ell\pm 1, n}\right) \right\} \left[1 + \frac{\phi^{IV}_{(a)} \left\{ \left(A_{\ell\ell} + \dots\right) e_{\ell n} e_{\ell n'} + \left(A_{\ell,\ell\pm 1} - \dots\right)\left(e_{\ell n} e_{\ell\pm 1, n'} + \dots\right) \right\}}{\phi''_{(a)} \left\{ e_{\ell n} e_{\ell n'} - \frac{1}{2}\left(e_{\ell n} e_{\ell\pm 1, n'} + e_{\ell n'} e_{\ell\pm 1, n}\right) \right\}} \right]^{-1} \quad (5.24)$$

and the choice of $e_{\ell n}$ as $e^0_{\ell n}$ corresponds to the assumption that the last [.....] is approximately constant, irrespective of the value of ℓ or of the choice of sign: this seems feasible but will not be studied further here.

$$A_{ll} = \frac{1}{nm}\sum_{h}^{(n)} \lambda_h e_{lh}^{o2} = \frac{1}{nm}\sum_{h}^{(n)} \lambda_h = A, \text{ say},$$

$$A_{l,l\pm1} = \frac{1}{nm}\sum_{h}^{(n)} \lambda_h e_{lh}^{o} e_{l\pm1,h}^{o} = \frac{1}{nm}\sum_{h}^{(n)} \lambda_h \cos\psi_h = B, \text{ say},$$

(5.25)

where A and B are independent of l [+]; further, we have

$$\left.\begin{aligned} \sum_{l}^{(n)} e_{lh}^{o} e_{l\pm1,h}^{o} &= \cos\psi_h \\ \sum_{l}^{(n)} e_{lh}^{o\,2} &= 1 \end{aligned}\right\}, \qquad (5.26)$$

the last since $[e_{lh}^{o}]$ is orthogonal. Thus the frequency equation becomes[++]

$$m\omega_h^2 = 2\phi''(a)(1-\cos\psi_h) + 4\phi^{iv}(a)(A-B)(1-\cos\psi_h)$$

$$= 4\sin^2(\tfrac{1}{2}\psi_h)\left\{\phi''(a) + 2\phi^{iv}(a)(A-B)\right\}, \qquad (5.27)$$

which is a direct generalisation of the usual equation for the ω_h^{o2}; however, A and B depend on a summation over all the frequencies $\omega_h\,(h=1\ldots n)$, since in (5.25) $\lambda_h = \frac{1}{2}\frac{E_h}{\omega_h^2}$ (E_h being the

+ These results are immediately confirmed by the equation (5.24), since the square bracket is now
$$[\ldots] = 1 + \frac{\phi^{iv}(a)}{\phi''(a)} \frac{2(A-B)(e_{lh}^{o2} - e_{lh}^{o} e_{l\pm1,h}^{o})}{(e_{lh}^{o2} - e_{lh}^{o} e_{l\pm1,h}^{o})},$$
which is independent of l.

++ The first term of (5.27) again confirms the values of e_{lh}^{o} used, since they are to transform the matrix $[\ldots]$ corresponding to this term into diagonal form, the latent roots being just these $\frac{4\phi''(a)}{m}\sin^2(\tfrac{1}{2}\psi_h)$.

vibrational energy, zero energy ϵ_{0n} plus thermal energy ϵ_{Tn}, of an oscillator of frequency ω_n), so that (5.27) is not a simple equation and provides the kind of "circular" dependence of lattice vibrations on their own total energy surmised in section 4a ; we have

$$A-B = \frac{1}{nm} \sum_{n}^{(n)} \frac{\sin^2(\frac{1}{2}\psi_n)}{\omega_n^2} \epsilon_n . \qquad (5.28)$$

It is clear from (5.27) that $\omega_n = \omega_{n-n}$, corresponding to the pairs of vectors $\{e^0_{sn}\}$, $\{e_{s,n-n}\}$ given in (5.10): physically, such a symmetrical result for opposite running waves in a regular chain is obviously necessary, and the $\{e^0_{sn}\}$ used here prescribe just such waves. The form of (5.27), (5.28) immediately suggests the solution+

$$\omega_n = \omega_m \sin(\tfrac{1}{2}\psi_n) , \qquad (5.29)$$

analogous to the $\omega_n^0 = \omega_m^0 \sin(\frac{1}{2}\psi_n)$ of the usual theory (with $m\omega_m^{02} = 4\phi''(a)$); we then have the equation for ω_m,

+ It is best to define ω_n directly, rather than its square as in the case of ω_n^0, ω_n^{02} which is properly determined through (or ω_m^{02}), since the equation for ω_m below is essentially cubic. We may also note that the definition still allows a rigid translation to correspond with $n=0$ and the usual vector $\{e^0_{s0}\}$, as we should expect.

$$\omega_m^2 = \omega_m^{0\,2} + \frac{1}{\omega_m^2}\,\frac{8\phi^{IV}(a)}{nm^2}\sum_h^{(m)} E_h \,. \qquad (5.30)$$

The total oscillator+ energy $E=\sum_h^{(m)} E_h$ falls into two parts, of which the zero energy $E_0=\sum_h^{(m)} E_{0h}$ is readily evaluated exactly,

$$E_0 = \sum_h^{(m)}\left(\tfrac{1}{2}\hbar\omega_h\right) = \frac{2m}{\pi}\left(\tfrac{1}{2}\hbar\omega_m\right), \qquad (5.31)$$

and the thermal energy $E_T=\sum_h^{(m)} E_{Th}$ can be approximated by a Debye integral++,

$$E_T^{\text{Debye}} = nkT\left\{\frac{1}{x_D}\int_0^{x_D} P(x)\,dx\right\}, \qquad (5.32)$$

where $P(x) = x/(e^x-1)$, $x=\dfrac{\hbar\omega}{kT}$, is Planck's thermal oscillator energy, and x_D is the appropriate upper limit -- see Section 5e.

Now in chapters 6 and 7 the linear chain will be needed in numerical applications of the theory to solid helium, the chain spacing being taken as the n/n distance in the helium lattice; for this $T\sim 10^{\circ}K$, and it will be seen below that $\omega_m \sim 1\times10^{13}\ \text{sec}^{-1}$: thus

+ This is the energy of the system of comparison oscillators invoked in the adaptation method -- cf. that of the non-harmonic chain itself as given below in 5d.

++ The Debye approximation to the zero energy E_0 is about $1{\cdot}25$ times the exact value,
$E_0^{\text{Debye}} = \dfrac{n\hbar}{\pi\omega_m}\displaystyle\int_0^{\omega_D}\omega\,d\omega = \frac{n\pi}{4}\left(\tfrac{1}{2}\hbar\omega_m\right) = \frac{\pi^2}{8}E_0$,
using $\omega_D=\pi/2\omega_m$, which reflects the difference between the Debye and the actual spectrum.

$$x_D = \frac{\pi}{2} x_m \sim \frac{\pi}{2} \frac{\Theta}{k} \times 10^{12} \sim 12.$$ +

A numerical integration of Planck's function gives the approximate values

x_D	5	6	7	8	9 and > 9	12
$\int_0^{x_D} P(x)\,dx$	1.60(3)	1.62(6)	1.63(7)	1.64(1)	1.64(3)	
$\frac{1}{x_D}\int_0^{x_D} P(x)\,dx$	.32(1)	.27(1)	.23(4)	.20(5)	.18(2) and less	.13(7)

so that in the case above $E_T^{\text{debye}} \sim \cdot 137\, nkT$, ++ and the ratio $\frac{E_T}{E_0} \sim \frac{\cdot 137\, nkT}{\frac{n}{\pi}\hbar\omega_m} = \frac{\cdot 137\,\pi^2}{2x_D} \sim \cdot 06$ -- it will never be more than $\sim \cdot 11$ in the cases considered. We may therefore reasonably neglect E_T in evaluating the energy which appears in (5.30), and so write this equation, using (5.31), as

$$\omega_m^2 = \omega_m^{o\,2} + \frac{1}{\omega_m}\left(\frac{8\hbar\phi^{IV}(a)}{\pi m^2}\right),$$

or

$$\omega_m^3 - \omega_m^{o\,2}\omega_m - \frac{8\hbar\phi^{IV}(a)}{\pi m^2} = 0, \qquad (5.33)$$

+ In the Oxford experiments (see Chap. 7), at the n/n spacing in the helium lattice corresponding to a molar volume of ~ 11 cc, the melting temperature is about 20°K, so that the smallest value of x_D is then ~ 9; at 20 cc, melting is at about 2°K, and the smallest value of x_D is then ~ 23.

++ The classical equipartition law gives nkT, about 8 times too big.

a simple cubic equation for the maximum lattice frequency ω_m .+

The cubic equation (5.33) is an example of the standard form $x^3 + 3Hx + G = 0$, with $3H = -\omega_m^{o2}$, $G = -\frac{8\pi\phi''(a)}{\pi m^2} < 0$, for which the discriminant is $G^2 + 4H^3 = \left(\frac{8}{m}\right)^2\left\{\left(\frac{\pi\phi''(a)}{\pi m}\right)^2 - \frac{4}{27}\frac{\phi''(a)^3}{m}\right\}$, using ω_m^{o2} as given above. Over the whole range of the parameter a corresponding to n/n distances in solid helium at molar volumes from about 10 cc upwards the discriminant can be shown to be positive++; this implies the existence of one real root only, the others being conjugate complex. The equations thus provide just the right number of real frequencies by which to define the set of stable harmonic oscillators proposed in the adaptation method, and this is

+ The equation (5.27) extends immediately to further neighbour interactions,
$$m\omega_m^2 = 4\sum_r \sin^2\left(\tfrac{r}{2}\psi_m\right)\left\{\phi''(ra) + 2\phi''(ra)(A - B_r)\right\}, \quad (5.34)$$
where $A - B_r = \frac{1}{mn}\sum_m^{(n)} \frac{\sin^2\left(\frac{r}{2}\psi_m\right)}{\omega_m^2}\epsilon_m$; assuming as a solution $\omega_m^2 = \sum_r b_r \sin^2\left(\frac{r}{2}\psi_m\right)$, $(b_r = \omega_m^2)$, in analogy to the usual formula (5.13), we would have instead of (5.30)
$$\sum_r\left[b_r - 4\left\{b_r^0 + \frac{8\phi''(ra)}{mn^2}\sum_m^{(n)} \frac{\sin^2\left(\frac{r}{2}\psi_m\right)}{\sum_r b_r \sin^2\left(\frac{r}{2}\psi_m\right)}\epsilon_m\right\}\right]\sin^2\left(\tfrac{1}{2}r\psi_m\right) = 0; \quad (5.35)$$
this equation for the b_r is not readily solved, even if all the brackets are positive, and therefore vanish.

++ Whenever $\phi''(a)$ is ≤ 0 (helium molar volumes $\geq \sim 15$ cc) the discriminant is obviously positive; numerical estimates based on the most probable helium potential $\phi(a)$ down to $a = a^o$, $\phi'(a^o) = 0$, at ~ 10 cc , show that the discriminant remains > 0 (see Chapter 6).

true at all helium volumes and probably for any other solids to which the theory might be applied; their frequencies are given by the formula $\omega_k = \omega_m \sin(\frac{1}{2}\psi_k)$, $k = 1 \ldots n$, where ω_m now refers to the real root of (5.33). When the $\phi^{iv}(a)$ term becomes small compared to the $\phi''(a)$ term ~~(as at the smallest molar volumes)~~ (5.33) reduces to the usual equation $\omega_m^2 = \omega_m^{o2}$, of which there is just the one real solution (choosing the + sign, say); near this limit the perturbation method (see below) provides a continuous transition from $\omega_m = \omega_m^o$ to the real solution ω_m of the non-linear equation. The complex solutions are without any physical significance.

To complete this non-linear lattice solution, we may use Cardan's method of solving (5.33), which gives by a well-known procedure the real root ω_m as $\omega_m = z_1^{\frac{1}{3}} + z_2^{\frac{1}{3}}$, z_1, z_2 being the two (real) roots of the quadratic equation $z^2 + Gz - H^3 = 0$:

$$z_1, z_2 = -\tfrac{1}{2}G\left\{1 \pm \sqrt{1 + \frac{4H^3}{G^2}}\right\},$$

$$\sim -\tfrac{1}{2}G\left\{2 + \tfrac{1}{2}\frac{4H^3}{G^2}, -\tfrac{1}{2}\frac{4H^3}{G^2}\right\}, \quad (5.36)$$

the latter when $\frac{4H^3}{G^2} \ll 1$, as it will be in the helium application. Explicitly, we have

$$-\tfrac{1}{2}G = \left(\frac{4k}{\pi m^2}\right)\phi^{iv}(a), \quad \frac{4H^3}{G^2} = -\left(\frac{4\pi^2 m}{27k^2}\right)\frac{\phi''(a)^3}{\phi^{iv}(a)^2}. \quad (5.37)$$

Near the inflexion point, where $\phi''(a) \sim 0$ and so $H \sim 0$, ω_m is directly dependent on the fourth degree terms :

$$\omega_m \sim \left\{ \frac{8k}{\pi m^2} \phi^{IV}(a) \right\}^{\frac{1}{3}} . \qquad (5.38)$$

Numerical calculations will be given in Chapter 6 .

The perturbation method of solving (5.22) treats the $\phi^{IV}(a)$ -term as small. For the zero-order solution we have

$$m\omega_m^{(0)2} \delta_{mm'} = \phi''(a^0) \sum_l \left\{ 2 e^0_{lm} e^0_{lm'} - \tfrac{1}{2} \sum_{+,-} \left(e^0_{lm} e^0_{l\pm1,m'} + e^0_{lm'} e^0_{l\pm1,m} \right) \right\}, \qquad (5.39)$$

where the spacing is taken as regular and equal to a^0 corresponding to the zero-order solution of the position equation[+], (5.15), which is to be made simultaneously; the $\omega_m^{(0)2}$, e^0_{lm} are then just those given in (5.10), (5.12) (both finite and cyclic cases are covered if l is suitably chosen) since (5.39) is the same as (6.7). The first order corrections to both the $\omega_m^{0\,2}$, e^0_{lm} follow from Born's general formulae (2.19,23); in the correction terms the values a^0 , $\omega_m^{(0)}$, e^0_{lm} are to be inserted, and simplifications similar to those in the work following (5.25) can be made. For example,

+ For the cyclic chain (5.15) holds identically, but the same a^0 is given by (5.52) below; $\omega^{(0)}$ implies that ω^0 is then reckoned at this spacing.

the frequency corrections[+] are

$$m(\omega_n^2)^1 = \sum_{ll'} u_{ll'}^1 e_{ln}^0 e_{l'n}^0$$

$$= a^1 \phi'''(a^0) \sum_l l \left\{ (e_{l+1,n}^0 - e_{ln}^0)^2 - (e_{ln}^0 - e_{l-1,n}^0)^2 \right\} +$$

$$+ \phi'''(a^0) \sum_l \left\{ 2A_{ll}^{(0)} e_{ln}^{0\,2} + \sum_{+,-} (A_{l,l\pm1}^{(0)} - 2A_{l,l\pm1}^{(0)}) e_{ln}^{0\,2} \right.$$

$$\left. + 2 \sum_{+,-} (A_{l,l\pm1}^{(0)} - A_{ll}^{(0)}) e_{ln}^0 e_{l\pm1,n}^0 \right\}, \qquad (5.40)$$

where the first bracket is just that appearing in (5.15), and the last just that of (5.23) except that $A_{ll'}^{(0)}$ is written to show that the argument involves the well known frequencies ω_n^0 at a^0. For the cyclic chain the previous work at once gives

$$m(\omega_n^2)^1 = 4a^1 \sin^2\left(\tfrac{1}{2}\psi_n\right) \left\{ a^1 \phi'''(a^0) + 2\phi'''(a^0)(A^{(0)} - B^{(0)}) \right\}, \qquad (5.41)$$

[+] The corrections e_{ln}^1 need not be considered further. Whether the wave-form is strictly preserved does not matter -- the object of the adaptation method is to compare energies with a system of oscillators, whatever the effective normal modes of vibration to which they correspond may be.

and the $\sin^2$ -form[+] of the frequency distribution is preserved; using (5.28) we have

$$m(\omega_n^{(0)}+\omega_n^{(2)})^2 = m\omega_n^{(0)2} + m(\omega_n^{(2)})^2$$

$$= 4\sin^2(\tfrac{1}{2}\psi_n)\left\{\phi''(a^0) + a^2\phi'''(a^0) + \frac{1}{2}\frac{E^{(0)}}{m}\frac{\phi^{iv}(a^0)}{\phi''(a^0)}\right\}, \qquad (5.42)$$

where $E^{(0)}/_m$ is the mean quadratic vibrational energy per particle corresponding to the positions a^0 ; the connection between the formulae (5.41,42) and the non-linear formula (5.27) is immediately obvious.

For the finite chain the simplifications can

+ The extension to further neighbours for this perturbation solution is immediate, in contrast to the non-linear case above. It is clear that each term

$$b_r^{(0)}\sin^2(\tfrac{r}{2}\psi_n) = 4\sin^2(\tfrac{r}{2}\psi_n)\phi''(ra^0)$$

of the usual formula (5.13) goes over into

$$(b_r^{(0)} + b_r^{(2)})\sin^2(\tfrac{r}{2}\psi_n) = 4\sin^2(\tfrac{r}{2}\psi_n)\left\{\phi''(ra^0) + ra^2\phi'''(ra^0) + 2\phi^{iv}(ra^0)(A^{(0)}-B_r^{(0)})\right\}, \qquad (5.43)$$

where (as in (5.34))

$$A^{(0)}-B_r^{(0)} = \frac{1}{nm}\sum_n^{(m)}\frac{\sin^2(\frac{r}{2}\psi_n)}{\omega_n^{(0)2}}E_n^{(0)}, \qquad \omega_n^{(0)2} = \sum_r b_r^{(0)}\sin^2(\tfrac{r}{2}\psi_n),$$

so that the various contributions to the frequency distribution all have their $\sin^2$-form preserved.

not be based on $\omega_n^{(0)} = \omega_{n-n}^{(0)}$, which is no longer true; the thermal expansion term $4\sin^2(\frac{1}{2}\psi_n)\alpha^2\phi''(a^0)$ is just the same as before (except for ψ_n of course), but the fourth degree terms are complicated to work out, since constant $A^{(0)}$ and $B^{(0)}$ do not appear; as there is no difficulty in principle, the work will not be carried any further here.

Higher approximations should not be made, since the terms neglected as small in the general theory (see 26) would then be of influence; the present thermal corrections are adequate to remove the difficulties of an expansion theory outlined in the introduction.

In the first of a series of papers on lattice stability Born (1940) has illustrated how in the case of a linear lattice long-wave (elastic) stability implies that all lattice frequencies are real. This depends on the conditions $b_1^0 > 0$, $b_2^0 \ldots < 0$, where the b_r^0 are defined in (5·13); in terms of the perturbation solution, exactly similar arguments will apply provided the b_r^1 defined in (5·43) satisfy the same inequalities. This seems likely to be the case, since the perturbation method is to

provide only small corrections and since it preserves the form of the frequency distribution: it is certainly the case when n/n interactions only are considered. The action of further neighbours in the non-linear solution is not readily obtained; we can do no more than apply the real n/n solution $\omega_m \sin(\frac{1}{2}qh)$ to solids under conditions in which they are known to be stable, and verify the results against observation.

5d: Thermodynamical Properties of the Linear Chain.

The general non-linear formulae given in chapter 3 for the thermodynamical functions involve the ratios

$$f_h = \frac{\omega_h^{o\,2}}{\omega_h^{\,2}} \quad ; \qquad (5.44)$$

for the usual quadratic theory quoted above $\omega_h^2 = \omega_h^{o\,2}$ and $f_h = 1$, while for the non-linear cyclic solution of the n/n linear chain -- no more general, nor finite, case will be used any further -- we have seen that the ratio $\omega_h^{o\,2}/\omega_h^2$ is independent of h ($\sin^2(\frac{1}{2}qh)$ terms cancel). We may therefore write

$$f_h = f = \frac{\omega_m^{o\,2}}{\omega_m^{\,2}} \qquad (5.45)$$

and this ratio of maximum frequencies is a function of the spacing (a) of the chain alone. When a has values close to a° , at the minimum $\phi'(a^\circ) = 0$, so that the anharmonic terms in the potential are of little influence, f will be a fraction approaching the value +1 of the usual theory; near the inflexion point $\phi''(a) = 0$, f is ~ 0 , the non-linear theory depending directly on the fourth-degree terms in the potential, and at any larger volumes f becomes more and more negative: the extreme value considered using the helium data in chapter 6, at a spacing corresponding to ~ 20 cc/mole, is $\sim -\cdot 7$.

The free energy can now be written

$$\mathcal{F} = n\phi(a) + \left\{\frac{f+3}{4}\right\}E_0 + \left\{\frac{f-1}{4}\right\}E_T + kT\sum_n \log\left(1 - e^{-h\nu_n/kT}\right), \tag{5.46}$$

which is to be compared with the usual $n\phi(a) + E_0 + kT\sum_n \log\left(1 - e^{-h\nu_n/kT}\right)$ of the harmonic theory. Since the first adaptation condition has been identically satisfied in this cyclic chain, we may regard (5.46) as a function of a variable parameter a , the lattice spacing, and impose the condition $\frac{\partial \mathcal{F}}{\partial a} = 0$ to determine it . The solution of this equation can be made by successive approximations if we consider the thermal terms as relatively

small, so that a is given in zero approximation by its value at $T = 0^\circ$ K; we have then to solve

$$\phi' + \left\{\frac{f+3}{4}\right\} e_0' + \frac{1}{4} f' e_0 = 0, \qquad (5.47)$$

where the argument a is understood, and e_0 is the zero energy per oscillator. This approximation is now determined through the quantum vibrational energy as well as the static potential, in accordance with the purpose outlined in the introduction; it may be contrasted with the zero-order solution of the perturbation method given below for the case in which $f \sim 1$, $\omega_m \sim \omega_m^0$.

The energy follows from $\mathcal{F}$:

$$\mathcal{E} = n\phi(a) + \left\{\frac{f+3}{4}\right\} E - \left\{\frac{f-1}{4}\right\} TC, \qquad (5.48)$$

where C is the specific heat at constant volume corresponding to the set of oscillators of energy E; this is to be compared with the usual $n\phi(a) + E$. The zero-point energy has the value

$$\mathcal{E}_0 = \left\{\frac{f+3}{4}\right\} E_0 = \left\{\frac{f+3}{4}\right\} \frac{2n}{\pi} \left(\tfrac{1}{2} h\omega_m\right), \qquad (5.49)$$

instead of the usual E_0; the e_0 quoted above is defined as

$$e_0 = \frac{E_0}{n} = \frac{2}{\pi} \left(\tfrac{1}{2} h\omega_m\right). \qquad (5.50)$$

and this ratio of maximum frequencies is a function of the spacing (a) of the chain alone. When a has values close to a° , at the minimum $\phi'(a^\circ) = 0$, so that the anharmonic terms in the potential are of little influence, f will be a fraction approaching the value +1 of the usual theory; near the inflexion point $\phi''(a) = 0$, f is ~ 0 , the non-linear theory depending directly on the fourth-degree terms in the potential, and at any larger volumes f becomes more and more negative: the extreme value considered using the helium data in chapter 6, at a spacing corresponding to ~ 20 cc/mole, is $\sim -\cdot 7$.

The free energy can now be written

$$\mathcal{F} = n\phi(a) + \left\{\frac{f+3}{4}\right\}E_0 + \left\{\frac{f-1}{4}\right\}E_T + kT\sum_n \log\left(1 - e^{-h\nu_n/kT}\right), \tag{5.46}$$

which is to be compared with the usual $n\phi(a) + E_0 + kT\sum_n \log\left(1 - e^{-h\nu_n/kT}\right)$ of the harmonic theory. Since the first adaptation condition has been identically satisfied in this cyclic chain, we may regard (5.46) as a function of a variable parameter a , the lattice spacing, and impose the condition $\frac{\partial \mathcal{F}}{\partial a} = 0$ to determine it . The solution of this equation can be made by successive approximations if we consider the thermal terms as relatively

the minimum condition $\frac{\partial \mathcal{F}}{\partial a} = 0$ is to be solved, in this case by successive approximations, to determine a. In zero order this gives

$$\phi'(a^0) = 0 \qquad (5.52)$$

the same equation as in the zero-order solution of the first adaptation condition for the finite chain, given in (5.18): in contrast to the non-linear case above, this value a^0 is the usual one determined by the static potential alone. The first-order correction to a^0 is got from

$$n\phi''(a^0)\, a^1 = -kT \sum_\nu \frac{\partial}{\partial a_1} \left\{ \log \left[2 \sinh \left(\frac{\hbar \omega_\nu^0(a)}{2kT} \right) \right] \right\}$$

$$= -\frac{1}{2} \frac{\phi'''(a^0)}{\phi''(a^0)} E^{(0)}, \qquad (5.53)$$

as is readily shown, $E^{(0)}$ being the total oscillator energy (based on the a^0). At low temperatures $E^{(0)} \sim E_0^{(0)} = \frac{2n}{\pi} \left(\frac{1}{2} \hbar \omega_n^{(0)} \right)$ and (5.53) becomes

$$a^1 = -\frac{\hbar}{\pi} \frac{\phi'''(a^0)}{\phi''(a^0) \sqrt{n \phi''(a^0)}}, \qquad (5.54)$$

just the same formula as appeared in (5.20'') of section 5b for the interior of a finite chain.

The free energy itself can now be expressed in terms of a^0, a^1 as

$$\mathcal{F} = n\phi(a^0) + kT\sum_w \log\left\{2\sinh\left(\frac{\hbar\omega_w^0(a^0)}{2kT}\right)\right\}$$

$$-\tfrac{1}{2}n\phi''(a^0)a^{1\,2} + \mathcal{F}^{2}_{(4)}(a^0), \qquad (5.55)$$

to the second order -- no term in a^2 appears since it would have the vanishing coefficient, $n\phi'(a^0)$. The extra term in $a^{1\,2}$ just replaces the vanishing third-degree quantity $\mathcal{F}^{2}_{(3)}(a^0)$ of the general theory. The perturbation formula for $\mathcal{F}$ in the case of a finite chain differs only in having various $a^1_{kl,\ell}$ instead of a^1 (see (5.20)), and this affects the now non-vanishing term $\mathcal{F}^{2}_{(3)}(a^0)$ alone: the changes in $\mathcal{F}$ produced by this involve only small energies of displacement at the ends, and are negligible in comparison with the size of the system.

5e: Elastic Properties of the Linear Chain.

For a cyclic elastic chain a procedure exactly analogous to that in 4c allows only those running waves for which γ is some point of the "cyclic mesh" defined by a spacing $\frac{1}{L}$ on the reciprocal axis, where L is the length of the specimen, $L = na$. Then the density of elastic waves is

$$dz = L\,dW = na\,dW, \qquad (5.56)$$

dW now being a line element along the reciprocal

axis. Corresponding to the three-dimensional $d\omega = \gamma^2 d\gamma\, d\Omega$, γ being the wave number and the solid angle $d\Omega$ allowing for all directions of propagation, we must here take $d\omega = 2d\gamma$, since waves may travel to the right or to the left. We then have the density

$$dz = \frac{na}{\pi c} d\omega \qquad (5.57)$$

where c is the elastic velocity and is such that $\omega = 2\pi\gamma c$. The Debye theory would in this case fix the maximum frequency ω_D according to

$$\left.\begin{aligned} n &= \int_0^{\omega_D} dz = \frac{na}{\pi c}\omega_D , \\ \omega_D &= \frac{\pi}{a} c , \end{aligned}\right\} \qquad (5.58)$$

and the Debye integrals are now

$$\frac{na}{\pi c}\int_0^{\omega_D} d\omega \ldots\ldots = \frac{n}{\omega_D}\int_0^{\omega_D} d\omega \ldots\ldots . \qquad (5.59)$$

These results have been quoted in 5c above; we should note that some care is needed in applying these integrals to ensure convergence at the origin.

The definition of the elastic properties of a linear lattice now reduces to that of the velocity c . This is equivalent to the single elastic constant c_{11} (or $\frac{1}{\kappa}$ in the general notation)

occurring in the equation for elastic waves,

$$\rho \ddot{u} = c_{11} \frac{\partial^2 u}{\partial x^2} , \qquad (5.60)$$

where ρ is the linear density n/a, since the relation

$$c = \sqrt{\frac{c_{11}}{\rho}} = \sqrt{\frac{1}{\rho \kappa}} \qquad (5.61)$$

follows immediately. According to the discussion of section 4a we could in this connection define the linear compressibility κ adiabatically from the energy $\mathcal{E}$. If t is the tension in the chain, defined by

$$t = \frac{1}{n}\left(\frac{\partial \mathcal{E}}{\partial a}\right)_S , \qquad (5.62)$$

we would then have

$$\frac{1}{\kappa} = a\left(\frac{\partial t}{\partial a}\right)_S = \frac{a}{n}\left(\frac{\partial^2 \mathcal{E}}{\partial a^2}\right)_S \qquad (5.63)$$

(a simpler formula than in the three-dimensional case where $\frac{\partial}{\partial V}$ is involved, V being proportional to a^3). Since the thermal effects in helium are known to be small at the temperatures with which we are concerned ($T \sim 10^\circ K$) the zero energy $\mathcal{E}_0$ could be used just as well in (5.63). Thus we would have

$$\frac{1}{\kappa} = a \frac{d^2}{da^2}\left\{\phi + \left\{\frac{f+3}{4}\right\}\varepsilon_0\right\} , \qquad (5.63')$$

the argument a again being understood, and from (5.61),

$$c = a\sqrt{\frac{\phi'' + \frac{1}{4}\{f''e_0 + 2f'e_0' + (f+3)e_0''}{m}} : \qquad (5.64)$$

this is a particular case of the general equation (4.17) of chapter 4. The derivatives of f and e_0 can be worked out in terms of those of the potential $\phi(a)$ and the new maximum lattice frequency $\omega_m(a)$.

In the particular case when $\phi''(a) \sim 0$ we have $f \sim 0$ and $\omega_m \sim \phi^{iv\,\frac{1}{3}}$ (see section 5c), and the formula (5.64) can be given explicitly. If we define a mean potential energy

$$v = \tfrac{1}{2} m a^2 \omega_m^2 \qquad (5.65)$$

it can be readily shown that

$$\left.\begin{aligned} e_0' &= \tfrac{1}{3} e_0 \frac{\phi^v}{\phi^{iv}}, \\ e_0'' &= \tfrac{1}{9} e_0 \frac{(3\phi^{iv}\phi^{vi} - 2\phi^{v\,2})}{\phi^{iv\,2}}, \end{aligned}\right\} \qquad (5.66)$$

and

$$\left.\begin{aligned} f' &= \frac{2a^2}{v}\phi''', \\ f'' &= \frac{2a^2}{3v}\frac{(3\phi^{iv\,2} - 4\phi^v\phi''')}{\phi^{iv}}. \end{aligned}\right\} \qquad (5.67)$$

The velocity c for this case will be worked out numerically in the next chapter with the help of a 6-12 Lennard Jones potential; it will be found that the final term $\frac{3}{4}\epsilon_0''$ is about twice as big as the sum of the other two ($\phi''(a) \sim 0$ here), which justifies to some extent the remarks made in 4d concerning the dependence of Θ_D on ϵ_0''.

The alternate procedure of section 4a defines the elastic velocity by equating it to the velocity of long lattice waves in the cyclic chain. From the formula (5.29) it is clear that

$$\omega_{(h\to 0)} \sim \omega_m(\tfrac{1}{2}\psi_h) \quad , \quad \psi_h = \frac{2\pi}{m}h \, ,$$

so that this velocity is given by, say,

$$c^* = \left(\frac{\omega_h}{2\pi\gamma_h}\right)_{h\to 0}$$

$$= \left(\frac{na\omega_h}{2\pi h}\right)_{h\to 0}$$

$$= \tfrac{1}{2}a\omega_m \, , \qquad (5.68)$$

where we use the cyclic relation $\gamma_h = \frac{h}{na}$ proved above[+]; numerical values of c^* will also be

+ These relations are well-known -- see, for example, Born & Göppert-Mayer (1933).

given in the next chapter.

We may remark that, with the velocity defined as c^*, the density of elastic waves given by (5.57) becomes

$$dz = \frac{2n}{\pi \omega_m} d\omega , \qquad (5.57')$$

and the maximum Debye frequency

$$\omega_D = \frac{\pi}{2} \omega_m , \qquad (5.58')$$

again well-known relations (e.g. Blackman, 1935).

There is no direct analytical equivalence between the velocities c, c^* defined above: any connection they have rests in the properties of the potential $\phi(a)$, and in the next chapter they will not be found in close numerical agreement. This bears out the supposition made in 4a that in the non-linear theory the virtual lattice waves need not coincide with the waves of elastic theory.

CHAPTER 6: CALCULATIONS BASED ON THE HELIUM LATTICE.

6a: The Helium Lattice.

The helium lattice is generally supposed to be of the close-packed hexagonal type. This is very similar to the close-packed (face-centred) cubic structure, which has obvious advantages for thermodynamical calculations -- it is based on one lattice parameter only, and the lattice sums are known (see Misra, 1940). We will use this cubic lattice throughout the present work, and it will be convenient to define its parameter a as the n/n distance in the lattice. The unit cell (containing one atom) then has the volume

$$\Delta = \frac{1}{\sqrt{2}} a^3 , \qquad (6.1)$$

and the cell vectors $\underline{a}_\alpha$ have the components

$$a\left(0, \frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}\right), \; a\left(\frac{1}{\sqrt{2}}, 0, \frac{1}{\sqrt{2}}\right), \; a\left(\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}, 0\right).$$

However, it is better to define the lattice coordinates $(l) = l_1, l_2, l_3$ along the cubic axes, and in terms of a cubic cell of side $\frac{a}{\sqrt{2}}$; the l_α must then be restricted so as to be either all even, or one even and two odd. This is essentially the scheme proposed by Born (1942), and is illustrated in the following figure.

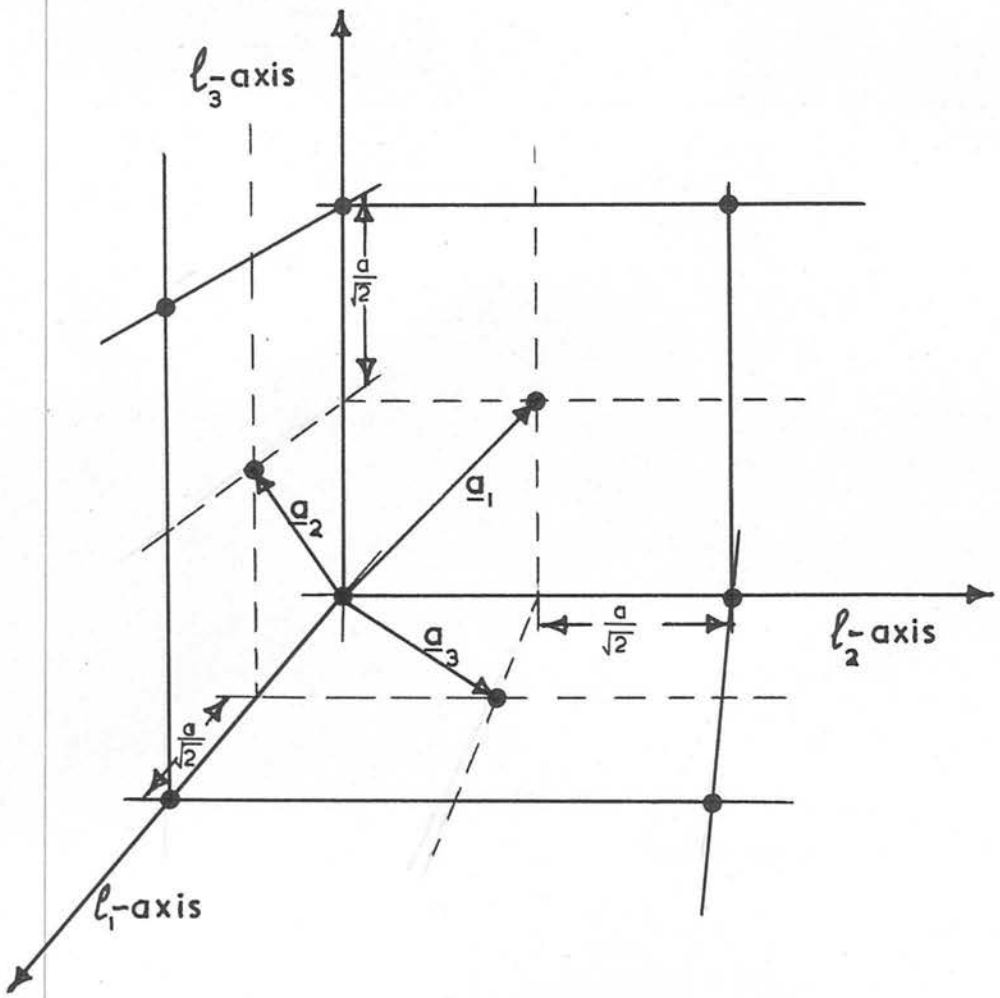


Fig. 6.1: Face-centred cubic structure.

The lattice vector $\underline{r}(l)$ then has the length

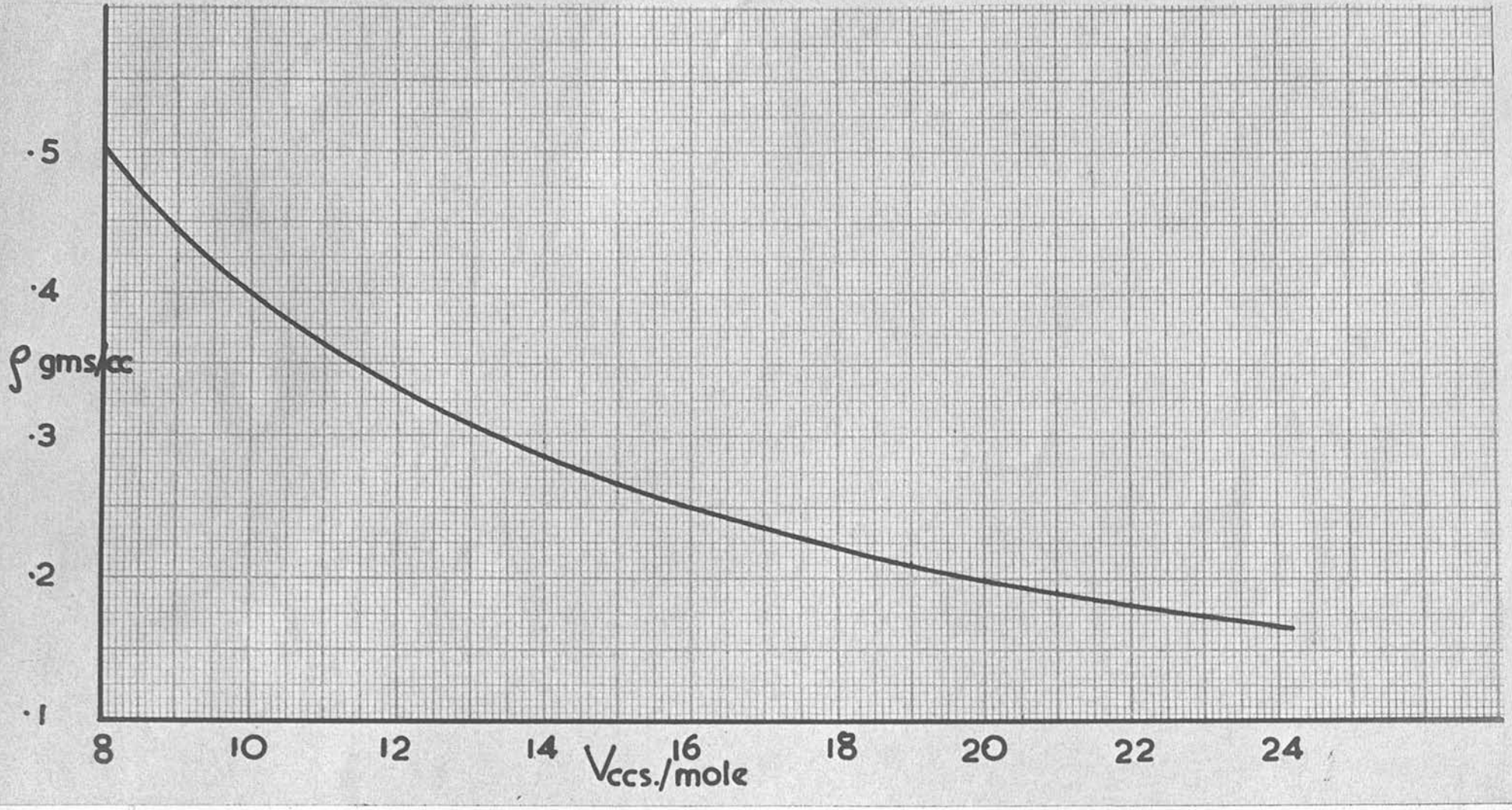
$$\underline{r}(l) = \frac{a}{\sqrt{2}} \left(l_1^2 + l_2^2 + l_3^2\right)^{\frac{1}{2}}$$

$$= \frac{1}{\sqrt{2}} a l, \qquad (6.2)$$

say, l being defined as the length of the vector (l_1, l_2, l_3). The molar volume is given by

$$V = N\Delta = \frac{1}{\sqrt{2}} N a^3, \qquad (6.3)$$

Fig. 6·3 : Density vs. molar volume.



and with $N = 6.03 \times 10^{23}$ and $a \sim 10^{-8}$ cm this can be written

$$V = 0.4265 \, (a \times 10^{8})^{3} \text{ cc.}; \qquad (6.3')$$

we may also express a in terms of V according to

$$a = 2^{\frac{1}{6}} \left\{ \frac{V}{N} \right\}^{\frac{1}{3}}, \qquad (6.4)$$

or

$$(a \times 10^{8}) = 1.33 \, V^{\frac{1}{3}} \text{ cms.}, \qquad (6.4')$$

with V measured in cc's.

The mass of a helium atom has the value

$$m = 6.7 \times 10^{-24} \text{ gm.}, \qquad (6.5)$$

and the density of solid helium is given by

$$\rho = \frac{m}{\Delta} = \sqrt{2} \, \frac{m}{a^{3}}; \qquad (6.6)$$

in molar quantities, this is

$$\rho = \frac{M}{V}, \qquad (6.6')$$

M having the value 4 grams. The density has been plotted against the molar volume in Fig. 6.3 .

We will consider the lattice energy on the basis of central forces, and write the total potential[+] Φ rather than $\mathcal{U}_{0}$ to indicate that we are

+ We shall write Φ hereafter for the undisplaced reference configuration (chosen as a lattice), dependent on macroscopic parameters alone.

speaking of a lattice solution of the general theory. If $\phi(r_\ell)$ is the elementary potential as in chapter 5, we at once have

$$\Phi = \tfrac{1}{2}N \sum_{(\ell)}{}' \phi(r_\ell)$$
$$= \tfrac{1}{2}N \sum_{(\ell)}{}' \phi\left(\frac{a\ell}{\sqrt{2}}\right) . \qquad (6.7)$$

Two types of interatomic potential ϕ have been proposed: the Lennard-Jones potential

$$\phi(a) = \phi_0 \frac{mn}{m-n}\left\{\frac{1}{m}\left(\frac{a_0}{a}\right)^m - \frac{1}{n}\left(\frac{a_0}{a}\right)^n\right\}, \qquad (6.8)$$

in which m, n are whole numbers and ϕ_0, a_0 (written instead of the previous a° for convenience), λ parameters of energy and length defining the minimum point, and a similar potential with an exponential repulsion factor

$$\phi(a) = \zeta e^{-\lambda a} - \frac{\mu}{a^b} - \frac{\nu}{a^\delta} , \qquad (6.9)$$

in which ζ , λ , μ , ν are constants to be determined. Both of these have the usual form, as shown in Fig. 6.2:

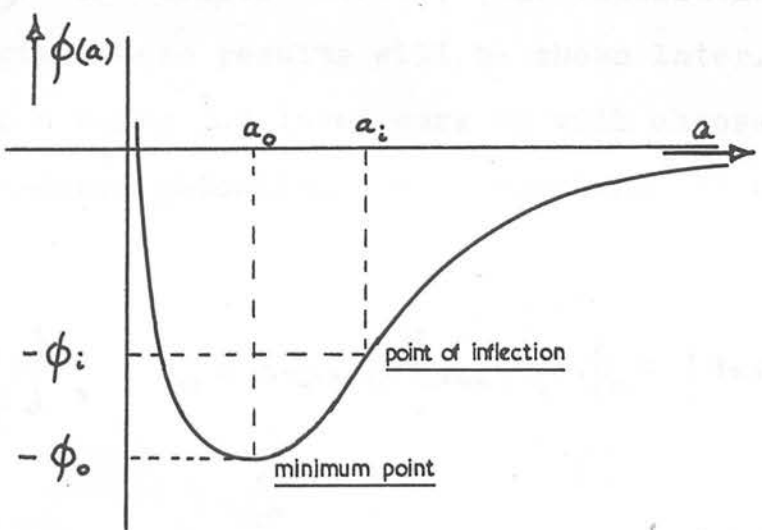


Fig. 6.2: The interatomic potential $\phi(a)$.

A full discussion of the determination of ϕ from measurements of the second virial coefficient of helium gas over a wide range of temperature has been given by Yntema and Schneider (1950). They find that neither of the usual choices $n=6$, $n=9$; $n=6$, $n=12$ for the Lennard-Jones potential can be fitted over the whole range, whereas the semi-empirical exponential formula can be made to give a good fit. However, in order to determine the new frequencies we require essentially the second and fourth derivatives of $\phi(a)$ in the region from the minimum up to and just beyond the inflexion point, and a 6–12 Lennard-Jones potential can be chosen to agree with the exponential reasonably well in this respect. In the table 6.1 have been listed values of the minimum parameters a_0 , ϕ_0 for these two potentials, as well as for those suggested by other authors, together with values of the derivatives $\phi''(a)$, $\phi^{IV}(a)$ at various volumes; the calculations which give these results will be shown later.

As a basis for later work we will choose a Lennard-Jones potential with parameters

$$\left.\begin{matrix} n=6 \\ n=12 \end{matrix}\right\} , \quad a_0 = 3.0\times10^{-8}\ \text{cm.} , \quad \phi_0 = 1.1\times10^{-15}\ \text{erg.}$$

(6.10)

Type of Potential	Author	$(r_0 \times 10^8)$ cms.	$(\phi_0 \times 10^{15})$ ergs.	10.61	11.99	13.72	14.90	18.31	21.08	Molar Volume (ccs)
				2.92	3.04	3.18	3.27	3.50	3.67	$(a \times 10^8)$ cms
Lennard-Jones:	Keesom (average)	2.8	1.2	41.5	9.5	-	-	-	-9.37	$\phi''(a)$ ergs/cm^2
				2.515	1.204	-	-	-	.0296	$(\phi^{iv}(a) \times 10^{-19})$ ergs/cm^4
	Fowler and Guggenheim	2.95	0.827	-	-	-	-	-	-	
n = 6	Yntema and Schneider	2.95	0.841	85.4	36.5	8.3	0	-6.9	-7.1	$\phi''(a)$ ergs/cm^2
n = 12				3.52	1.792	.782	.456	.116	.036	$(\phi^{iv}(a) \times 10^{-19})$ ergs/cm^4
	Chosen to agree with exponential	3.0	1.1	150.8	66.0	20.5	6.17	-7.83	-9.12	$\phi''(a)$ ergs/cm^2
				5.76	2.986	1.306	.782	.205	.069	$(\phi^{iv}(a) \times 10^{-19})$ ergs/cm^4
Exponential	Yntema and Schneider	3.0	1.15	151.7	68.6	19.8	3.4	-9.8	-10.9	$\phi''(a)$ ergs/cm^2
				5.02	2.76	1.34	.820	.204	.068	$(\phi^{iv}(a) \times 10^{-19})$ ergs/cm^4

Table 6.1 : The interatomic potential $\phi(a)$ for solid helium.

Yntema and Schneider give the constants in their exponential formula to be

$$(\zeta \times 10^{15}) = 1.2 \times 10^{6} \quad \text{ergs},$$

$$(\mu \times 10^{15}) = 1240 \quad \text{ergs},$$

$$(\nu \times 10^{15}) = 1890 \quad \text{ergs},$$

$$\lambda = (0.212)^{-1}, \qquad (6.11)$$

the distance a in this case being measured in Ångstrom units.

For the Lennard-Jones potential the total lattice energy (6.7) can be written as

$$\Phi(a) = \tfrac{1}{2} N \phi_0 \frac{mn}{m-n} \left\{ \frac{(\sqrt{2})^m}{m} S_m \left(\frac{a_0}{a}\right)^m - \frac{(\sqrt{2})^n}{n} S_n \left(\frac{a_0}{a}\right)^n \right\}$$

$$= \frac{A}{m} \left(\frac{a_0}{a}\right)^m - \frac{B}{n} \left(\frac{a_0}{a}\right)^n, \qquad (6.12)$$

where a is the n/n distance, as defined above; S_p is Misra's lattice sum

$$S_p = \sum_{(l)}{}' \, l^{-\frac{p}{2}} \qquad (6.13)$$

and the meaning of the constants A , B is clear.

If we define the ratio

$$s = \left(\frac{a_0}{a}\right)^{n-m} \qquad (6.14)$$

(6.12) becomes

$$\Phi(a) = s^{\frac{n}{n-m}} \left\{ \frac{A}{m} - s \frac{B}{n} \right\}. \qquad (6.12')$$

For the particular parameters chosen above we require the sums

$$\left.\begin{aligned} S_6 &= 1.8067 \\ S_{12} &= 0.1896 \end{aligned}\right\}, \qquad (6.13')$$

and s is simply $\left(\frac{a_0}{a}\right)^6$: then the lattice potential can be readily evaluated from the formula

$$\Phi(a) = s \left\{ \frac{A}{m} - s \frac{B}{n} \right\}$$

$$= -1.268 s \left\{ 1.807 - 0.757 s \right\} \times 10^2 \text{ cals/mole}; \qquad (6.12'')$$

some values are given in tables 6.3, 6.4, and $\Phi(a)$ is shown graphically in fig. 7.7 .

For the exponential potential the total lattice energy (6.7) becomes

$$\Phi(a) = \tfrac{1}{2} N \left\{ \zeta \sum_{(l)}{}' \left(e^{-\lambda a}\right)^{\frac{l}{12}} - \mu S_6 \left(\frac{r_2}{a}\right)^6 - \nu S_8 \left(\frac{r_2}{a}\right)^8 \right\}, \qquad (6.15)$$

where ζ_6 , ζ_8 are again Misra's sums, with

$$\zeta_8 = 0{\cdot}8001 \,. \qquad (6{\cdot}13'')$$

Starting from any atom as origin, we get for the permitted coordinates (ℓ) corresponding to first, second, ... neighbours the values of ℓ shown in table 6.2. Now, according to the value of λ quoted above, it is clear that $\lambda a \sim 15$ ($a \sim 3\text{Å}$) so that $e^{-\lambda a} \sim 10^{-6}$ -- explicit values will be given below -- and the factors $(e^{-\lambda a})^{\frac{\ell}{\sqrt{2}}}$ for successive neighbours can be readily estimated. The first few terms of the lattice sum

$\zeta \sum'_{(\ell)} (e^{-\lambda a})^{\frac{\ell}{\sqrt{2}}}$, each calculated according to the corresponding number of atoms, are also shown in table 6.2. It is clear that we may neglect the terms due to all but first neighbours with reasonable accuracy, so that the lattice sum $\sum_{(\ell)}$ gives the contribution

$$\tfrac{1}{2} N \cdot 12 (\zeta \times 10^{15}) e^{-\lambda a} \times 10^{-15} \text{ ergs}$$

to the potential Φ . The approximation made has, in fact, negligible effect since the sum of the second and third terms in Φ is of the order ten times larger than the exponential part. With the help of the values of ζ_6, ζ_8 given above the whole expression for Φ can now be

Order of Neighbours	(ℓ)	Number of Neighbours	ℓ	$\frac{\ell}{\sqrt{2}}$	$\left(e^{-\lambda a}\right)^{\frac{\ell}{\sqrt{2}}}$	$\zeta\Sigma\left(e^{-\lambda a}\right)^{\frac{\ell}{\sqrt{2}}}$
1st	0, ±1, ±1 ±1, 0, ±1 ±1, ±1, 0	12	$\sqrt{2}$	1	$\sim 10^{-6}$	$\sim 1.4\times10^{-14}$ erg.
2nd	0, 0, ±2 0, ±2, 0 ±2, 0, 0	6	2	$\sqrt{2}$	$\sim 10^{-8.5}$	$\sim 2.3\times10^{-17}$ erg.
3rd	±1, ±1, ±2 ±1, ±2, ±1 ±2, ±1, ±1	24	$\sqrt{6}$	$\sqrt{3}$	$\sim 10^{-10.4}$	$\sim 1.2\times10^{-18}$ erg.
–	– – –	– – –	etc.	– – –	– – –	– – – –

Table 6.2 : Lattice coordinates and the exponential $\phi(a)$.

written

$$\Phi(a) = Ce^{-\lambda a} - \frac{D}{a^6} - \frac{E}{a^8}$$

$$= \tfrac{1}{2}N\left\{12(1.2\times10^6)e^{-\lambda a} - 14.45\left(\frac{1240}{a^6}\right) - 12.80\left(\frac{1890}{a^8}\right)\right\}\times10^{-15} \text{ ergs}$$

$$= 7.215\{\ldots\ldots\ldots\ldots\} \text{ cals/mole.} \qquad (6.15')$$

the constants following from (6.11). Values of $\Phi(a)$ according to this exponential formula are also given in table 6.3, and shown graphically in fig. 7.7 ; it will be seen that the chosen Lennard-Jones interaction gives a rather deeper lattice potential than is got from the exponential.

It is of interest to calculate the critical volumes at which the lattice potential Φ has its minimum and inflexion points, together with the corresponding energies, on the basis of the two chosen interactions. These volumes define n/n distances, which may be compared with the minimum (a_0) and inflexion (a_i) distances of the elementary potential $\phi(a)$ (as in fig. 6.2). The differences illustrate, in this connection, the effect of assuming only n/n interactions to be of importance -- in which case $\Phi(a)$ is merely proportional to the elementary potential $\phi(a)$;

V ccs.	$(a \times 10^8)$ cms.	$s = \left(\frac{a_0}{a}\right)^6$	$12(5 \times 10^{15})\frac{1}{a^{12}}$ ergs — a in Angstroms.	$1445\left(\frac{1240}{a^6}\right)$	$1280\left(\frac{1890}{a^8}\right)$	$-\Phi(a)$ Lennard-Jones cals/mole	$-\Phi(a)$ Exponential cals/mole
10.61	2.92	1.175	15.12	28.92	4.56 .	136.8	132.2
11.99	3.04	.925	8.64	22.68	3.32	129.8	126.1
13.72	3.18	.708	4.45	17.34	2.32	114.2	109.7
14.90	3.27	.602	2.87	14.73	1.85	103.3	98.8
18.31	3.50	.399	.984	9.76	1.08	76.2	71.0
21.08	3.67	.300	.432	6.24	.735	60.2	47.2

Table 6.3 : * Calculation of the helium lattice potential.

* The particular volumes chosen here are those at which specific heat measurements have been made - see chapter 7.

the comparison is made in table 6.4.

From the formula (6.12') we may write

$$\Phi'(a) = -\frac{1}{a} s^{\frac{m}{m-n}} \{A - sB\},$$

$$\Phi''(a) = \frac{1}{a^2} s^{\frac{m}{m-n}} \{(m+1)A - s(n+1)B\}, \qquad (6.16)$$

and these vanish when

$$A - s_0 B = 0 ,$$

$$(m+1)A - s_i(n+1)B = 0 , \qquad (6.17)$$

say. For our particular choice of Lennard-Jones interaction, (6.17) defines volumes V_0, V_i and energies Φ_0, Φ_i as given numerically in table 6.4.

From the exponential formula (6.15') we may write

$$\Phi'(a) = -\lambda C e^{-\lambda a} + \frac{1}{a}\left\{6\frac{D}{a^6} + 8\frac{E}{a^8}\right\},$$

$$\Phi''(a) = \lambda^2 C e^{-\lambda a} - \frac{1}{a^2}\left\{42\frac{D}{a^6} + 72\frac{E}{a^8}\right\}; \qquad (6.18)$$

the volumes and energies corresponding to the solutions of these equations are also shown in table 6.4.

	$\Phi'(a) = 0$		$\phi(a) = 0$		$\Phi''(a) = 0$		$\phi''(a) = 0$	
	L-J	Exp.	L-J	Exp.	L-J	Exp.	L-J	Exp.
V ccs.	10.57 (V_o)	10.57	11.50	11.40	14.39 (V_i)	14.24	15.75	15.33
($a \times 10^8$) cms.	2.91	2.91	3.00 (a_o)	2.99	3.24	3.22	3.33 (a_i)	3.30
$-\Phi(a)$ cals/mole.	137 (Φ_o)	133	133	130	108 (Φ_i)	105	95.6	94.5
$-(\phi(a) \times 10^{15})$ ergs.	1.06	1.10	1.10 (ϕ_o)	1.13	.958	.964	.866 (ϕ_i)	.887

Table 6.4 : Comparison of the critical points of $\Phi(a)$, $\phi(a)$.

Yntema and Schneider have remarked in their paper that data on the crystallographic form of solid helium will determine the minimum parameter a_0 . The usual theory would say that observations of crystal structure fix the $\Phi'(a) = 0$ configuration, so that from the minimum lattice volume V_0 the distance a_0 can be deduced according to the form of $\phi(a)$. This is not true, since the lattice must correspond to the average positions under quantum vibrations, and for helium even at $T = 0^\circ K$ the relatively large zero energy ε_0 will define a wider spacing. The non-linear solution for a , as illustrated for the linear chain by (5.47), must be used in the deduction of the elementary parameter a_0 from the observations.

The volume V_i is the one at which the normal quadratic theory breaks down completely, since the frequencies, proportional to $\Phi''(a)$, there become negative; its value, ~ 14 cc/mole from table 6.4, is near the middle of the range quoted in chapter 4 in the discussion of Domb's results, and to be used in chapter 7.

6b: The Derivatives of $\phi(a)$.

In order to give a numerical discussion of the linear-chain solutions derived in chapter 5, the results of which will be used in approximating to the helium data in chapter 7, we need the various derivatives of $\phi(a)$ with respect to its argument a . They will be given firstly for the general Lennard-Jones potential, from which those for the particular 6-12 potential chosen in 6a follow at once, and secondly for the exponential potential.

If we write

$$s^{(p)} = \frac{(m+p-1)!}{m!} - s\frac{(n+p-1)!}{n!} , \quad p = 0,1,2\ldots, \tag{6.19}$$

where s is given in (6.14),
and define

$$\psi = \phi_0 \frac{mn}{m-n} , \tag{6.20}$$

then it follows at once that

$$\left.\begin{aligned} \phi(a) &= \psi\, s^{\frac{m}{n-m}}\, s^{(0)} \\ \phi'(a) &= -\psi\, s^{\frac{m}{n-m}}\, \frac{s^{(1)}}{a} \\ \phi''(a) &= \psi\, s^{\frac{m}{n-m}}\, \frac{s^{(2)}}{a^2} \\ &\cdots\cdots\cdots \end{aligned}\right\} ; \tag{6.21}$$

the whole variation of each derivative with a is exhibited in the s -factors and the power of a^{-1} . For the chosen 6-12 potential we have numerically

$$\left.\begin{aligned} s &= \left(\frac{a_0}{a}\right)^6 , \\ s^{\underbrace{m}_{m=m}} &= s , \\ s^{(p)} &= \frac{(p+5)!}{6!} - s\,\frac{(p+11)!}{12!} , \end{aligned}\right\} \quad (6.22)$$

together with

$$\psi = -1.32 \times 10^{-14} \text{ erg.}$$

In table 6.5 are given, at various volumes, the values of the s -factors sufficient to determine up to the sixth derivative of the Lennard-Jones potential.

If in the exponential formula (6.9) we write

$$\left.\begin{aligned} \mu^{(p)} &= \frac{(p+5)!}{5!} \\ \nu^{(p)} &= \frac{(p+7)!}{7!} \end{aligned}\right\} , \quad p = 0, 1, 2, \ldots \quad (6.23)$$

V_{ecs}	$(a \times 10^8)$ cms	s	$(s^{(0)} \times 10)$	$s^{(1)}$	$s^{(2)}$	$(s^{(3)} \times 10^{-2})$	$(s^{(4)} \times 10^{-3})$	$(s^{(5)} \times 10^{-4})$	$(s^{(6)} \times 10^{-5})$
10.57	2.91	1.192	+0.67	-0.19	-8.49	-1.61	-2.75	-4.71	-8.31
10.61	2.92	1.175	+0.69	-0.18	-8.28	-1.58	-2.70	-4.64	-8.17
11.50	3.00	1.000	+0.83	0	-6.00	-1.26	-2.23	-3.87	-6.88
11.99	3.04	0.925	+0.90	+0.08	-5.02	-1.12	-2.02	-3.54	-6.32
13.72	3.18	0.708	+1.08	+0.29	-2.22	-0.73	-1.43	-2.59	-4.71
14.39	3.24	0.642	+1.13	+0.36	-1.35	-0.61	-1.25	-2.30	-4.21
14.90	3.27	0.602	+1.17	+0.40	-0.83	-0.53	-1.14	-2.13	-3.92
15.75	3.33	0.538	+1.22	+0.46	0	-0.42	-0.97	-1.85	-3.45
18.31	3.50	0.399	+1.33	+0.60	+1.82	-0.17	-0.59	-1.24	-2.41
21.08	3.67	0.300	+1.42	+0.70	+3.10	+0.01	-0.32	-0.81	-1.68

Table 6.5 : Properties of the chosen Lennard-Jones potential.

it may be readily shown that

$$\left.\begin{aligned}
\phi(a) &= (\zeta e^{-\lambda a}) - \left\{\left(\frac{\mu}{ab}\right) + \left(\frac{\nu}{a\beta}\right)\right\} \\
\phi'(a) &= -\lambda(\zeta e^{-\lambda a}) + \frac{1}{a}\left\{\mu^{(1)}\left(\frac{\mu}{ab}\right) + \nu^{(1)}\left(\frac{\nu}{a\beta}\right)\right\} \\
\phi''(a) &= \lambda^2(\zeta e^{-\lambda a}) - \frac{1}{a^2}\left\{\mu^{(2)}\left(\frac{\mu}{ab}\right) + \nu^{(2)}\left(\frac{\nu}{a\beta}\right)\right\} \\
&\text{- - - - - - - - - -}
\end{aligned}\right\}; \qquad (6.24)$$

the whole dependence on a is now directly shown. In addition to the quantities in round brackets, which have already appeared in (6.15'), we need powers of λ and the various $\mu^{(\varphi)}$, $\nu^{(\varphi)}$: the latter are given in table 6.6, again sufficient to determine the sixth derivative of the potential.

The values of the derivatives in the two cases are compared in table 6.7; the most important are $\phi''(a)$, $\phi^{(v)}(a)$, which determine the linear frequencies, and have already been quoted in table 6.1; the choice of the particular Lennard-Jones potential was made there on the basis of these two derivatives.

p	$\mu^{(p)}$	$v^{(p)}$
1	6.00	8.00
2	4.20 x 10	7.20 x 10
3	3.36×10^2	7.20×10^2
4	3.02×10^3	7.92×10^3
5	3.02×10^4	9.50×10^4
6	3.32×10^5	1.24×10^6

Table 6.6: Factors in the Exponential $\phi(a)$.

Facing p. 6.21.

V ccs.	$(a \times 10^8)$ cms.	$-(\phi(a) \times 10^{15})$ ergs. L-J.	Exp.	$(\phi'(a) \times 10^8)$ ergs/cm L-J.	Exp.	$(\phi''(a) \times 10^{-1})$ ergs/cm^2 L-J.	Exp.	
10.57	2.91	1.06	1.09	-10.3	-10.1	15.78	15.89	
10.61	2.92	1.07	1.10	- 9.56	- 8.42	15.08	15.17	
11.50	3.00	1.10	1.13	0	1.08	8.81	9.06	
11.99	3.04	1.10	1.11	3.21	3.82	6.60	6.86	
13.72	3.18	1.01	1.01	8.52	9.70	2.05	1.98	
14.39	3.24	.958	.948	9.41	10.50	1.09	.830	
14.90	3.27	.930	.926	9.71	10.95	.617	.340	
15.75	3.33	.867	.854	9.82	10.61	0	-.200	
18.31	3.50	.700	.677	9.02	9.63	-.783	-.980	
21.08	3.67	.562	.569	7.55	7.88	-.912	-1.09	

Table 6.7 : Derivatives of the

$-(\phi'''(a)\times10^{-9})$ ergs/cm^3		$(\phi^{iv}(a)\times10^{-18})$ ergs/cm^4		$(-\phi^{v}(a)\times10^{-27})$ ergs/cm^5		$(\phi^{vi}(a)\times10^{-36})$ ergs/cm^6	
L-J.	Exp.	L-J.	Exp.	L-J.	Exp.	L-J.	Exp.
103	100	60.4	52.1	35.5	26.0	21.5	12.58
98.6	94.9	57.6	50.2	34.9	25.0	20.4	12.12
61.6	61.5	36.4	33.4	21.0	16.9	12.5	8.23
48.7	50.3	29.9	27.6	16.6	14.1	9.78	6.88
21.2	22.4	13.1	13.4	7.45	7.04	4.26	3.50
15.2	15.3	9.62	9.73	5.46	5.18	3.08	2.60
12.0	12.3	7.82	8.20	4.52	4.39	2.54	2.21
8.09	8.43	5.60	6.00	3.21	3.30	1.80	1.68
2.09	1.93	2.05	2.04	1.24	1.38	.690	.727
-.08	-.05	.688	.680	.482	.530	.272	.361

interatomic potential, $\phi(a)$.

6c: Frequencies in the Linear Chain.

We will consider a linear lattice having its spacing equal to the n/n distance in solid helium, and composed of helium atoms; this will be of use in providing an elastic velocity which we can take as an approximation to the average elastic velocity in the helium lattice, as well as in illustrating the general non-linear theory.

According to section 5c, the linear-chain frequencies are given (see (5.29), (6.36)) by

$$\left.\begin{aligned} \omega_k &= \omega_m \sin\left(\tfrac{1}{2}\psi_k\right) \\ \omega_m &= z_1^{\frac{1}{3}} + z_2^{\frac{1}{3}} \end{aligned}\right\}$$

where

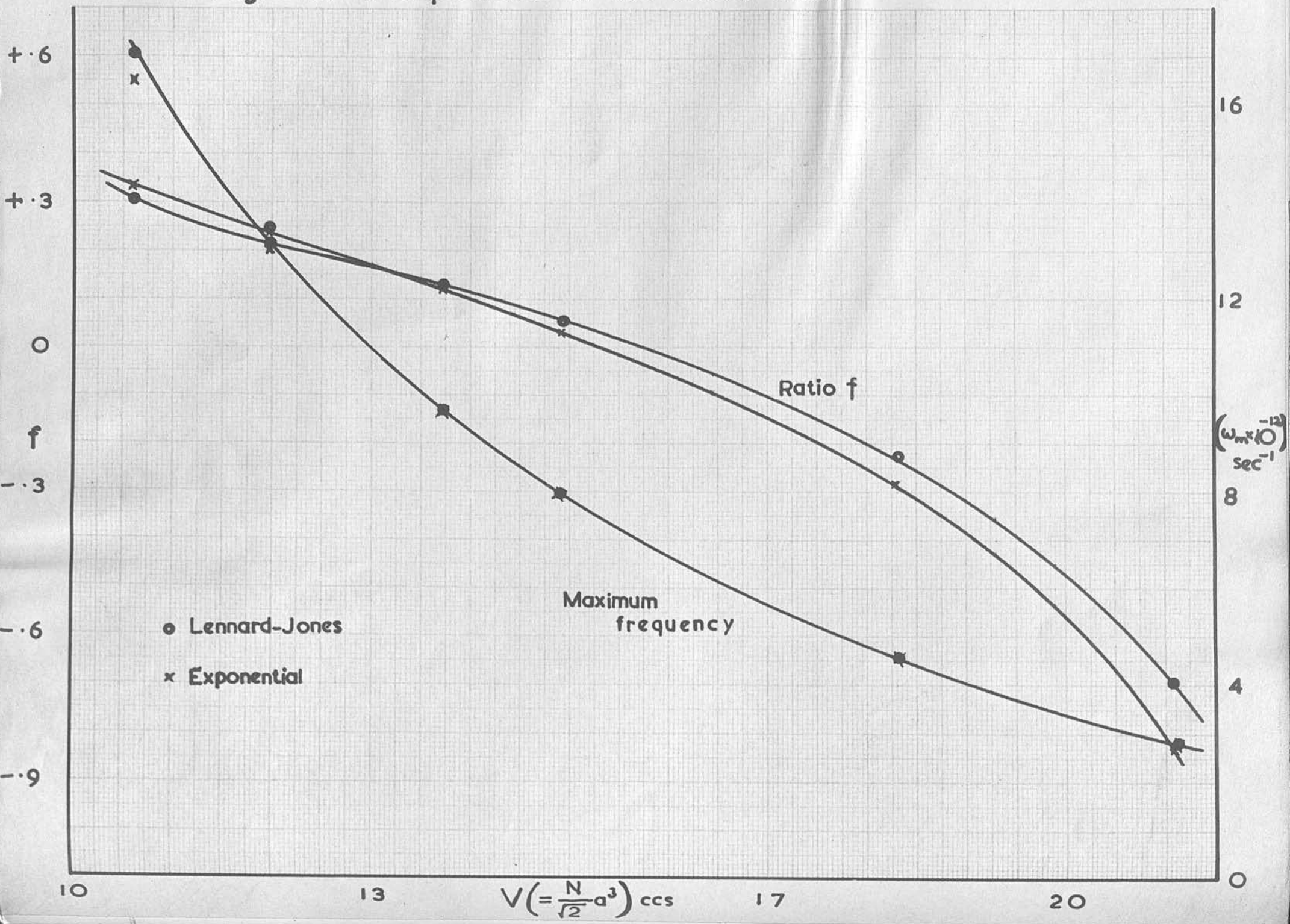
$$z_1, z_2 = \left(\frac{4k}{\pi m^2}\right)\phi^{(iv)}(a)\left\{1 \pm \sqrt{1-\left(\frac{4\pi^2 m}{27k^2}\right)\frac{\phi^{(ii)}(a)^3}{\phi^{(iv)}(a)^2}}\right\}.$$

With the mass of a helium atom as given in (6.5) we have for the two constants

$$\left(\frac{4k}{\pi m^2}\right) = 2.98 \times 10^{19},$$

$$\left(\frac{4\pi^2 m}{27k^2}\right) = 8.89 \times 10^{30}. \qquad (6.25)$$

Fig. 6·4: Frequencies in the linear chain.



From the values of table 6.7 it is clear that $\left(\frac{4\pi^2 m}{2\gamma k^2}\right) \frac{\phi''(a)^3}{\phi^{iv}(a)^2} \sim 10^{-3}$ or less, so that the expanded values given in (5.36) are justified:

$$z_1 = \left(\frac{4\pi}{\pi m^2}\right)\phi^{iv}(a)\left\{2 - \frac{1}{2}\left(\frac{4\pi^2 m}{2\gamma k^2}\right)\frac{\phi''(a)^3}{\phi^{iv}(a)^2}\right\},$$

$$z_2 = \left(\frac{4\pi}{\pi m^2}\right)\phi^{iv}(a)\left\{\frac{1}{2}\left(\frac{4\pi^2 m}{2\gamma k^2}\right)\frac{\phi''(a)^3}{\phi^{iv}(a)^2}\right\};$$

in fact, the second term in z_1 can on the whole be neglected. In the particular case $\phi''(a) \sim 0$ it is clear that $\omega_m \sim z_1^{\frac{1}{3}}$, as quoted in section 5c. Numerical values of z_1, z_2 and ω_m are given in table 6.8 at various spacings, together with the corresponding helium molar volumes: their derivation from (5.36) and the values of table 6.7 presents no difficulty. The maximum frequency ω_m is shown in fig. 6.4.

The ratio of frequencies

$$f = \frac{\omega_n^{0\,2}}{\omega_n^2} = \frac{\omega_m^{0\,2}}{\omega_m^2}$$

defined in section 5d has also been shown in table 6.8 and fig. 6.4; its numerical values follow

V	$(a \times 10^{8})$	$(\alpha_1 \times 10^{-38})$		$(\alpha_2 \times 10^{-35})$		$(\omega_m \times 10^{-12})$ sec^{-1}		f	
ccs.	cms.	L-J	Exp.	L-J	Exp.	L-J	Exp.	L-J	Exp.
10.61	2.92	34.2	29.9	78.3	92.0	17.04	16.50	+.309	+.333
11.99	3.04	17.8	16.5	26.7	15.5	13.50	13.00	+.216	+.242
13.72	3.18	7.78	7.98	.876	.767	9.64	9.70	+.132	+.126
14.90	3.27	4.66	4.89	.039	.006	7.91	7.97	+.059	+.032
18.31	3.50	1.22	1.22	-.618	-.611	4.56	4.56	-.225	-.282
21.08	3.67	.413	.408	-2.93	-2.53	2.79	2.81	-.698	-.825

Table 6.8 : Maximum frequencies in the linear chain.

from the definition (5.10) according to the relation

$$f = \frac{4\phi''(a)}{m\omega_m^2} = 0.597 \frac{\phi''(a)}{(\omega_m \times 10^{-12})^2} \quad (6.26)$$

This linear-chain f will be used as an approximation to the various f in the helium lattice, and it can be shown that its values do not depend very sensitively on the particular parameters chosen in $\phi(a)$.

The exponential potential $\phi(a)$ will not be considered any further; it is clear from the tables so far given that the chosen Lennard-Jones potential will do just as well in thermodynamical applications.

6d: Elastic velocities in the Linear Chain.

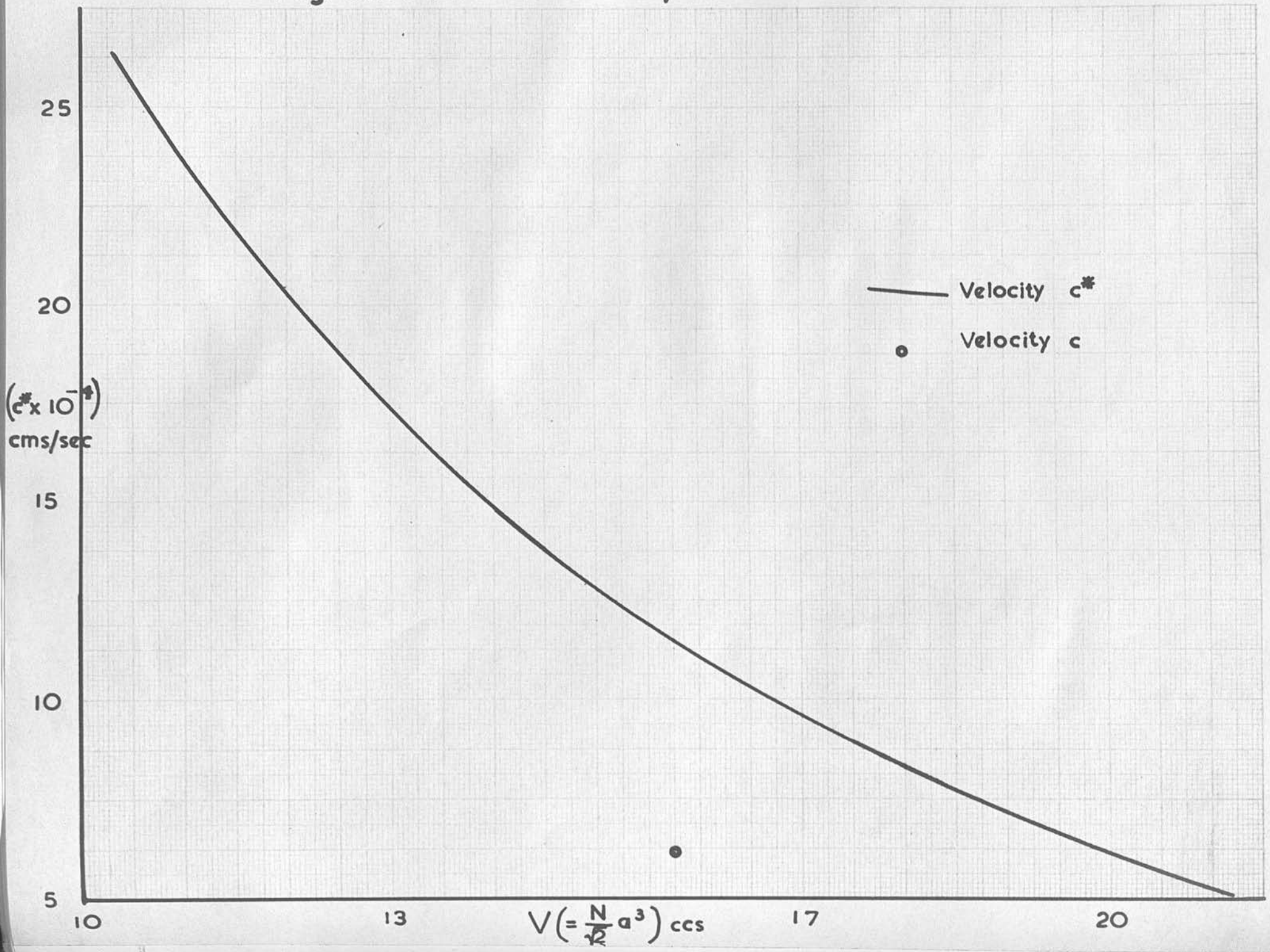
The velocity c^* defined by (5.68),

$$c^* = \tfrac{1}{2} a \omega_m ,$$

is readily evaluated from the values of table 6.8; the result is given in table 6.9 and shown graphically in fig. 6.5.

The adiabatic formula for the velocity

Fig. 6.5: Elastic velocity in the linear chain.



F 6.25

V ccs.	$(a \times 10^{8})$ cms.	$(c^{*} \times 10^{-4})$ cms/sec.	$(c \times 10^{-4})$ cms/sec.
10.61	2.92	24.88	
11.99	3.04	20.48	
13.72	3.18	15.32	
14.90	3.27	12.92	
15.75	3.33	~ 11.5	6.13
18.31	3.50	7.97	
21.08	3.67	5.12	

Table 6.9: Elastic Velocities in the Linear Chain.

(5.64) is not readily handled in general terms; we would have to work out the first and second derivatives of f and ρ_0 using generalisations of the expressions (5.38) and (5.45); in addition, values of $\omega_{m}''(a)$ at various volumes are required. These could be obtained graphically, and a study of fig. 6.4 gives a general indication of the variation to be expected.

In the region $\phi'(a) \sim 0$ $(f \sim 0)$ we may use the simple expressions obtained in chapter 5, with values

of the derivatives of the Lennard-Jones potential $\phi(a)$ got from table 6.7. We then find, at 15.75 cc,

$$\begin{aligned} \sigma &= 1.82 \times 10^{-13} \text{ ergs}, \\ e_0 &= 2.35 \times 10^{-15} \text{ ergs}, \\ e_0' &= -4.34 \times 10^{-7} \text{ ergs/cm}, \\ e_0'' &= 76.3 \text{ ergs/cm}^2, \\ f' &= -1.003 \times 10^{8} \text{ cm}^{-1}, \\ f'' &= -9.60 \times 10^{16} \text{ cm}^{-2}, \end{aligned} \qquad (6.27)$$

so that

$$c_{(f=0)} = a\sqrt{\frac{(f''e_0 + 2f'e_0' + 3e_0'')}{4m}}$$

$$= 6.13 \times 10^{4} \text{ cm/sec}. \qquad (6.28)$$

The ratio of the final term in c to the sum of the other two is ~ 2, so that the variation of c with volume may be expected to depend mainly on the term in e_0''; however this

velocity will not be worked out here for other volumes, just the particular value obtained above being shown in table 6.9.

CHAPTER 7 : THERMAL PROPERTIES OF SOLID HELIUM.

7a: General Comparison of Theory and Experiment.

In a recent thesis[+] Dugdale (1951) has described very full experiments on the thermal properties of solid helium in the temperature range from about $4^\circ K$ to $24^\circ K$; the basic measurement was of the specific heat at constant volume, and this experimental quantity will be written here[++] $b_v^{exp}(T)$; some of the results are plotted in fig. 7.1[+++]. In 7b we will be able to choose, on the basis of the non-linear theory, functions $b_v(T)$ which coincide almost exactly with the experimental values except for the last few degrees below the melting point, the divergence being most apparent in the case of small molar volumes, where (at melting) it is some 5% of the value of b_v . Such curves are shown superimposed on the experimental points in fig. 7.1.

+ I am much indebted to Professor F.E. Simon of Oxford for making a copy of this thesis available.

++ All the specific heats to be considered here are at constant volume; the suffix v is not meant to imply this, but to emphasise that a function depends on the volume as well as on its other arguments.

+++ The scale on which the specific heat figures are drawn is such that the experimental errors are less than can be represented.

Fig 7.1 : Specific heat of solid helium as a function of T.

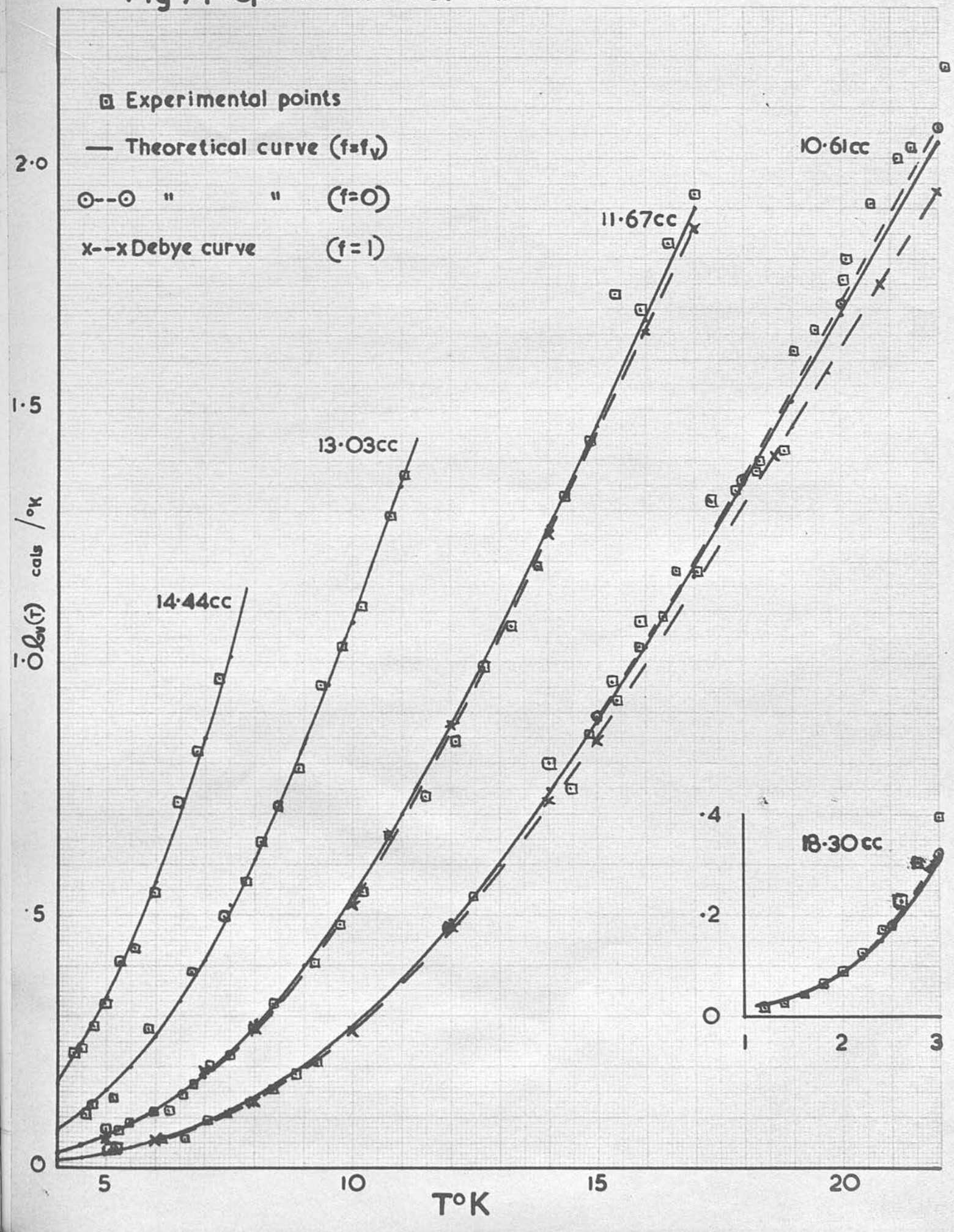
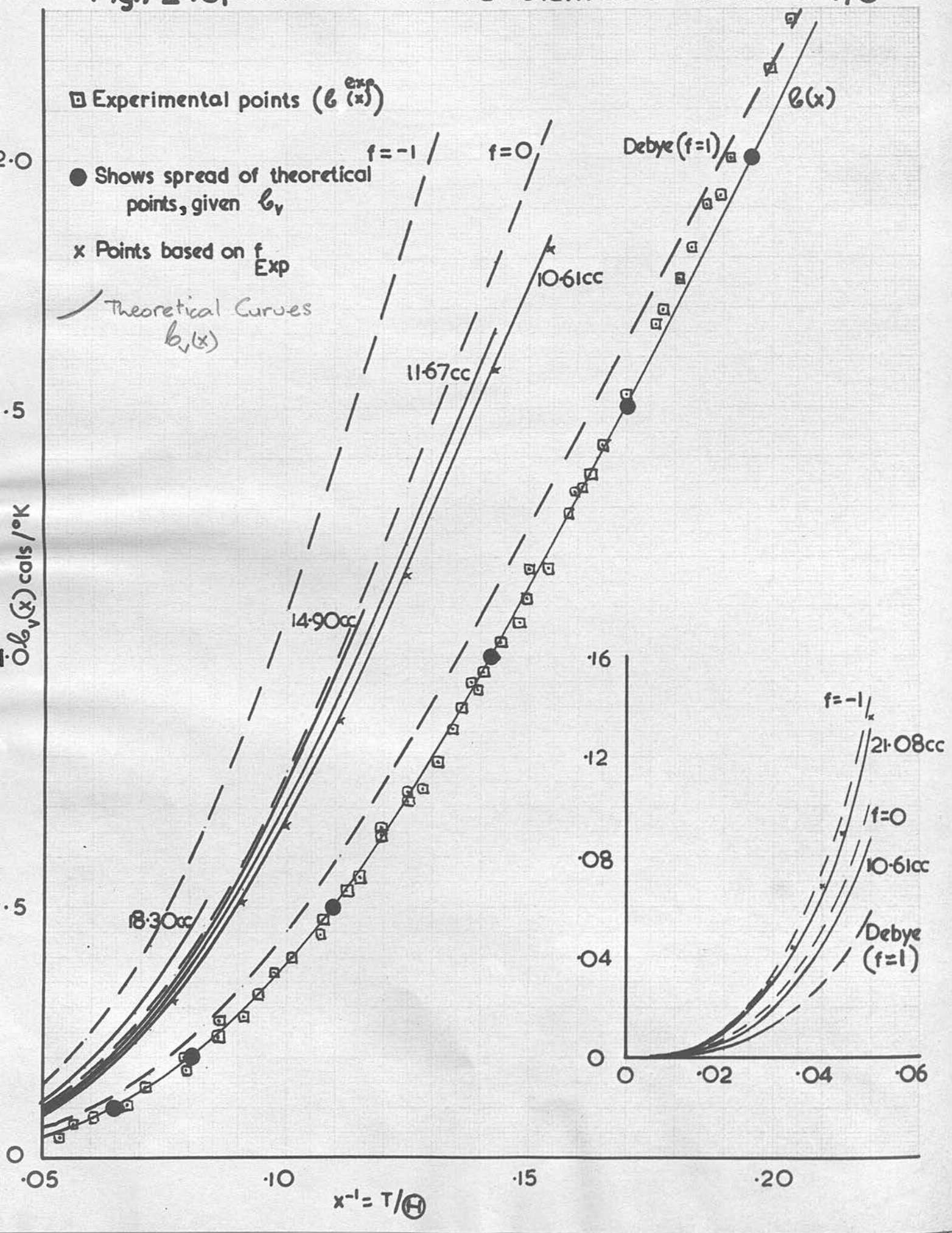


Fig.7·2 : Specific heat of solid helium as a function of T/Θ

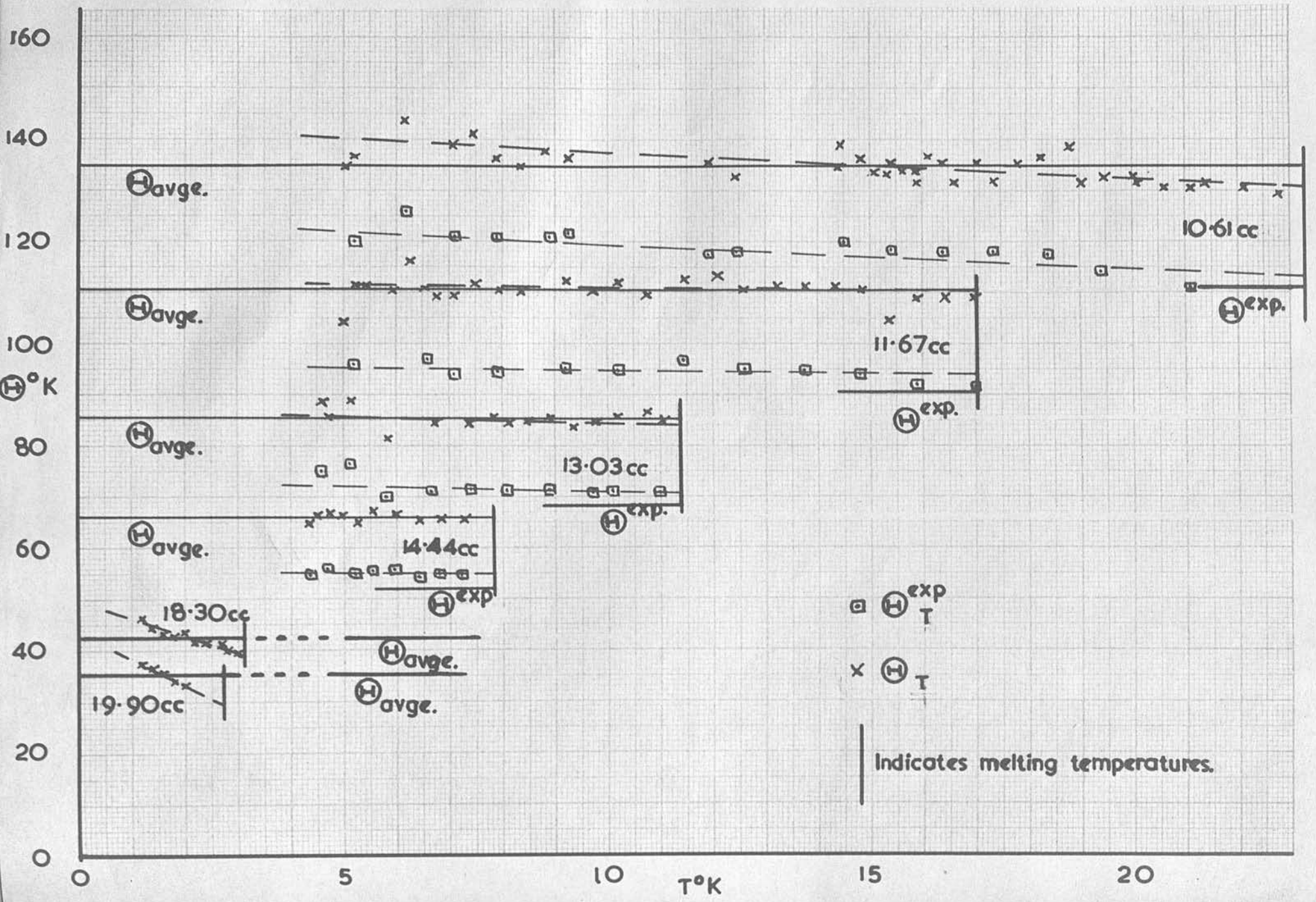


P 7·2

Dugdale found that the $b_v^{exp}(T)$ curves could be accurately reduced to a single curve $b^{exp}(x)$ if characteristic temperatures θ^{exp} were chosen at each volume, with $x = \frac{\theta}{T}$; see fig. 7.2. The universal reduced curve is <u>not</u> the Debye curve[+], which is much flatter; the difference is indicated in the figure. A similar reduction can be made, with the same accuracy, for the theoretical curves, the result again diverging from Dugdale's in the fashion described above. However, the resultant single curve $b(x)$ does not arise directly in the non-linear theory, which provides instead various curves $b_v(x)$, functions of x <u>and volume</u>; it is surprising that they in turn can be empirically superimposed, as the result implies (see also 7b below). Some of these curves are drawn in fig. 7.2; their dependence on volume is due to the ratios $f = \frac{\omega_0^2}{\omega^2}$ introduced in chapter 3. The theoretical expressions for the $b_v(x)$, given in 7b, demonstrate clearly the divergence from Debye's formula and reduce to it in the limiting case to which the harmonic theory applies.

+ Defined by the function $C(x)$ quoted in (4.25) Dugdale shows more than one Debye curve as a function of x , apparently in error.

Fig. 7·3 : Debye Θ as a function of T.



F. 7·3

Dugdale has chosen the absolute values of Θ^{exp} by fixing $\Theta = 100°K$ to correspond with $V = 11.05$ cc : this is stated to agree with the experimental specific-heat Debye parameter+ Θ_T^{exp} at $T = 0°K$, based on very low temperature measurements by Wilkinson & Wilks (1951). In fact, from the values of Θ_T^{exp} given by Dugdale, and shown in fig. 7.3, it appears that the chosen Θ^{exp} (see also fig. 7.3) are nearer to the $\Theta_{T_m}^{exp}$ on the melting curve (with $T = T_m \sim 20°K$ at 11 cc) and given in table 7.2 below; Domb (1951) also quotes them as his Θ_∞ (see chapter 4), along the melting curve. However, the variation of Θ_T^{exp} at constant volume is relatively small (see fig. 7.3), and, which is more important, the ratios of the Θ_T^{exp} at various volumes are roughly constant as the temperature varies, sufficiently so to allow the superposition of specific heat curves to be made; the absolute values chosen for Θ^{exp} do not matter very much in this connection.

In the non-linear theory the $\Theta_D(V)$ which

+ This is got, as mentioned in 4d, by making the Debye formula $C_v(x)$ agree with the experimental results at every T and V .

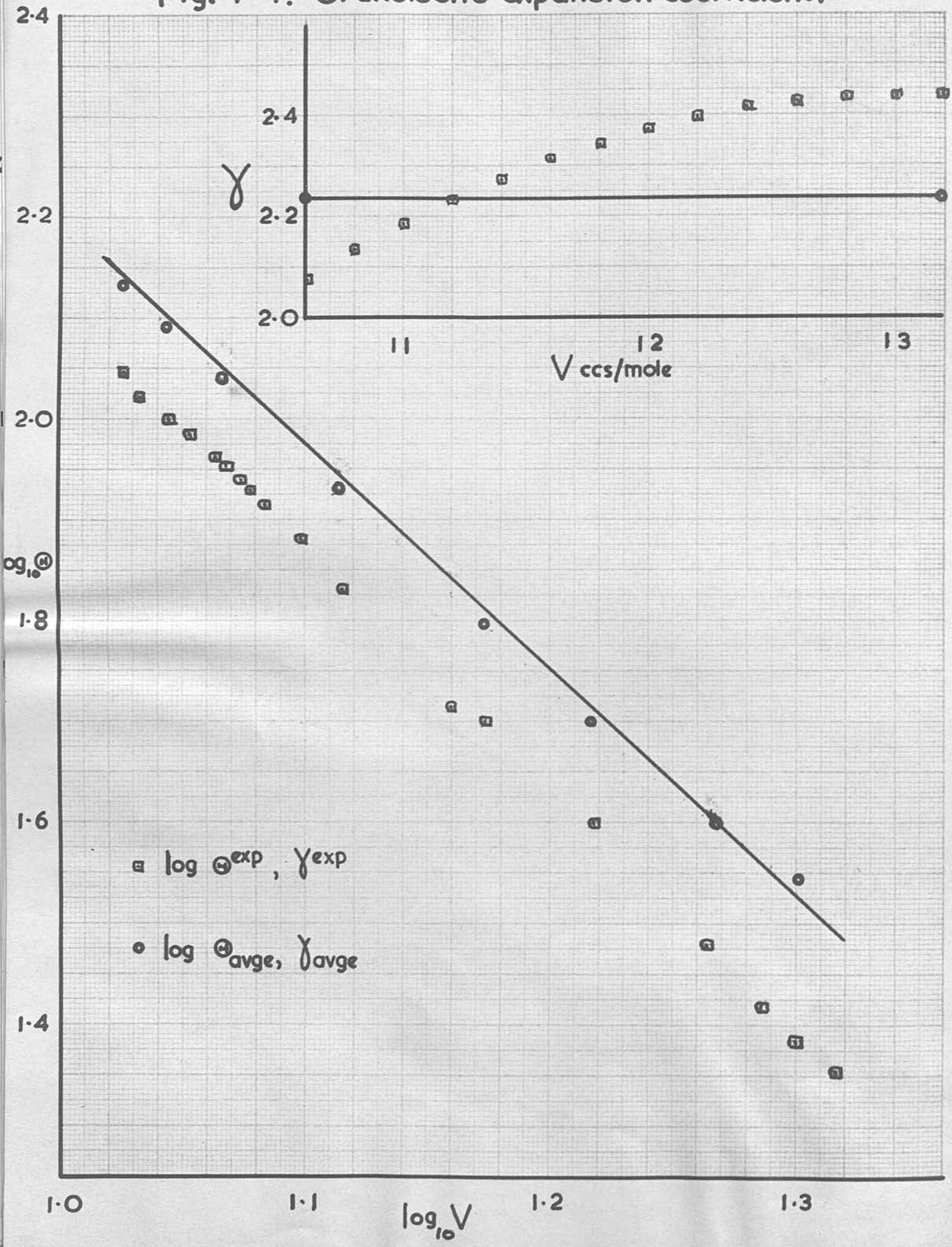
occur in each function $b_v(x)$ ought in principle to be got from elastic considerations according to the definitions of chapter 4: an approximation to this will be made in 7c, where we use the linear elastic velocities of chapters 5 & 6, but it does not provide very satisfactory nor conclusive results. Otherwise, various Θ_T can be calculated to make the $b_v(x)$ curves fit the specific heat data, and an average parameter Θ_{avge} can then be derived for each volume; this will be done numerically in 7b, and forms the basis for the theoretical curves shown in fig. 7.1. The procedure is analogous to the usual fitting of Debye curves mentioned above. Such Debye curves do not agree with the points of 7.1 as well as the fitted theoretical curves, as is to be expected from the above discussion - some examples are included in fig. 7.1; what is more to the point is that these directly determined Debye curves are not really relevant to the non-linear theory at all.

It will be found that the Θ_{avge} (at different volumes) do not stand in the same ratio as Dugdale's Θ^{exp}, which is closely the ratio of the parameters necessary in reducing the theoretical $b_v(T)$ curves to $b(x)$; this is just another way of saying that the theory

requires, not one, but several curves in terms of the reduced variable x, which have in turn to be superimposed; numerical values will be given in 7b, table 7.2. In fact the Θ_T, Θ_{avge} of the theory are quite distinct from Dugdale's empirical parameters Θ_T^{exp}, Θ^{exp} and consequences of this will be discussed in 7c; the Θ_T, Θ_T^{exp} have, however, much the same temperature dependence, the curves of fig. 7.2 not differing greatly in shape: this is also shown in fig. 7.3. Since the temperature variation of Θ_T is small, as mentioned for Θ_T^{exp}, there is no very significant trend in the partial average $\Theta - S$ which can be formed over successive ranges of temperature at each volume; it is only in the very low temperature range $1-3\,^{\circ}K$, where some results of Keesom are quoted, that the averaging process is not very satisfactory (see again fig. 7.1). The Θ_{avge} used in deriving the curves of fig. 7.1 refer to the whole range of temperature in each case (e.g. from $5-23\,^{\circ}K$ at $10{\cdot}61$ cc); they are indicated in fig. 7.3.

The volume dependence of Dugdale's Θ^{exp} is compared in fig. 7.4 with that of the Θ_{avge}, with a view to fixing Grüneisen's coefficient

Fig. 7·4: Grüneisen's expansion coefficient.



$$\gamma = -\frac{d\log\Theta}{d\log V} .$$

Dugdale has shown how well-known thermodynamical identities based on a universal $b(x)$ curve lead to the relation

$$\gamma = \frac{\alpha V}{\kappa b_v}$$

quoted in chapter 4: this empirical result avoids any reference to non-linearity in the theory, and is here to be interpreted in terms of the Θ^{exp}, b^{exp}. Since the theoretical $b_v(x)$ curves can also be superposed to give a universal $b(x)$, the same empirical relation is allowed by the theory; but γ is not to be defined directly from the Θ_{avge}, and must in fact be approximately the same as γ^{exp} (since the theoretical reduction of the $b_v(T)$ curves is approximately the same as the experimental). Values of γ^{exp} are shown in the figure, and those of the γ_{avge} (corresponding to our Θ_{avge}) are included for comparison.

Of the remaining thermodynamical properties discussed by Dugdale we will consider the zero energy (ε_0) and the lattice energy (Φ). The values given by the non-linear theory for ε_0

are much the same as those of Dugdale (see fig. 7.6 below), even though the Debye parameters are very different in the two cases: both sets of Θ -values have been chosen to give the right specific heats and it is not unreasonable to suppose they will give approximately equivalent zero energies, even though the ordinary Debye formula is not theoretically correct. From the internal energy at $T=0°K$, derived thermodynamically by Dugdale from the empirical $\Theta^{exp}(x)$ values, Φ follows by the subtraction of ε_0 : the values obtained from the non-linear ε_0 above are much the same as those of Dugdale (see fig. 7.7 below).

In regard to melting, Dugdale has shown that the Lindemann formula

$$\frac{T_m^{\frac{1}{2}}}{\Theta V^{\frac{1}{3}}} = \text{constant} \qquad (7.0)$$

remains true; as he remarks, this result is surprising, since Lindemann's considerations were only a rough approximation to the ordinary harmonic theory. It was also shown by Domb (1951) that the mean square displacement of the lattice particles is not proportional to $V^{\frac{2}{3}}$ in the case of helium, which relation was the basis of Lindemann's

formula. These two numerical results also follow from the non-linear theory, as will be given in the next section, and a rather better fit between helium and the other inert gas solids is obtained.

7b: Numerical Determination of the Specific Heat.

In chapter 3, by the application of Debye's isotropic approximation to the spectrum of (virtual) harmonic oscillations in the non-linear theory, we have been able to write the specific heat at constand volume as

$$C_v(x) = C_D(x) - \frac{3}{4}\left\{1 - F_v(x,T)\right\}\left\{C^E(x) - C_D(x)\right\}, \tag{7.1}$$

where $C_D(x)$ is Debye's specific heat function,

$$C_D(x) = 3R\left\{4D(x) - 3P(x)\right\}, \tag{7.2}$$

and $C^E(x)$ is Einstein's specific heat function,

$$C^E(x) = 3R\left\{P(x) - x\,\frac{dP(x)}{dx}\right\}. \tag{7.3}$$

The volume dependent ratio $f_v(x,T)$ introduced there (really a function of ω_D, where $x = \frac{\omega_D}{T}$) was an average over the three branches of the acoustic spectrum. These are not known for the general helium lattice, and we will approximate to f by using the function f_v derived for the linear chain in the last chapter, V specifying the helium lattice volume which determines the chain spacing. This f_v was shown to be constant along the frequency spectrum, the property $f'(\xi) \sim 0$ postulated in chapter 3, and its value was defined in terms of ω_m, the maximum linear lattice frequency.

From tables of the functions $C(x)/3R$ (see Fowler & Guggenheim (1939)) and $C^E(x)/3R$ (see Mayer & Mayer (1947)) the quantities $C(x)$, $\frac{3}{4}\{C^E(x) - C(x)\}$ have been calculated: they are given in table 7.1. For the various volumes, and corresponding f_v, given in table 6.8, the quantities $f_v \cdot \frac{3}{4}\{C^E(x) - C(x)\}$ have been calculated, and finally the specific heats $C_v(x)$; these are also shown in table 7.1, and plotted in figure 7.2.

The difference, at any one volume, between the f_v as calculated from the two interaction

$x = \frac{\Theta}{T}$	$\frac{1}{x} = \frac{T}{\Theta}$	$C_v(x)$ cals/mole ($f=1$)	$-\frac{3}{4}\{C^E_v(x) - C_v(x)\}$ cals/mole	$\delta_v(x) = C_v(x) - \{1-f_v\}\frac{3}{4}\{C^E_v(x) - C_v(x)\}$		
				V: 10.61 cc		11.99 cc
				f: .309 (L-J)	.333 (Exp.)	.216
4	.250	2.992	.887	3.605	3.584	3.687
5	.200	2.192	.881	2.801	2.780	2.883
6	.167	1.580	.784	2.122	2.093	2.195
7	.143	1.137	.654	1.589	1.573	1.650
8	.125	.822	.518	1.180	1.167	1.228
9	.111	.604	.408	.886	.876	.924
10	.100	.452	.321	.674	.666	.704
11	.091	.344	.249	.515	.510	.538
12	.083	.267	.196	.403	.398	.421
13	.077	.211	.156	.319	.315	.333
14	.072	.169	.127	.257	.253	.268
15	.067	.138	.103	.209	.206	.218
16	.0625	.113	.0848	.172	.169	.179
17	.0589	.0946	.0709	.144	.142	.150
18	.0556	.0797	.0598	.121	.120	.127
19	.0527	.0678	.0509	.103	.102	.107
20	.0500	.0577	.0433	.088	.087	.092
21	.0477	.0502	.0376	.076	.075	.080
23	.0445	.0381	.0286	.058	.057	.060
25	.0400	.0297	.0223	.045	.045	.048
27	.0371	.0236	.0177	.036	.036	.038
29	.0345	.0191	.0143	.029	.029	.030
33.3	.0300	.0125	.0094	.019	.019	.020
40	.0250	.0073	.0055	.011	.011	.012
50	.0200	.0037	.0028	.006	.006	.006
66.6	.0150	.0016	.0012	.002	.002	.003
100	.0100	.0005	.0004	.001	.001	.001

Table 7.1 : Theoretical

$$b_v(x) = C_v(x) - \{1 - f_v\}^{\frac{3}{4}} \{C^{\infty}(x) - C(x)\}$$

13.72 cc	14.90 cc	18.31 cc	21.08 cc		For Comparison	
.132	.059	-.225	-.698 (L-J)	-.825 (Exp.)	0	-1
3.762	3.827	4.078	4.498	4.611	3.879	4.766
2.959	3.022	3.271	3.688	3.799	3.073	3.954
2.261	2.318	2.540	2.912	3.010	2.364	3.148
1.705	1.753	1.938	2.247	2.330	1.791	2.445
1.272	1.310	1.456	1.702	1.768	1.340	1.858
.958	.988	1.103	1.296	1.349	1.012	1.420
.731	.755	.845	.997	1.038	.773	1.094
.560	.578	.647	.765	.797	.593	.841
.438	.452	.507	.600	.625	.463	.660
.347	.358	.402	.476	.496	.367	.523
.279	.288	.323	.383	.399	.296	.423
.227	.234	.263	.312	.325	.241	.344
.185	.192	.216	.256	.267	.198	.283
.156	.161	.180	.214	.223	.166	.237
.132	.136	.152	.180	.188	.140	.199
.112	.115	.129	.153	.160	.118	.170
.096	.099	.110	.131	.136	.101	.144
.082	.085	.095	.113	.118	.088	.126
.063	.065	.072	.085	.089	.067	.095
.050	.051	.057	.067	.070	.052	.074
.039	.040	.045	.053	.055	.041	.059
.032	.033	.036	.043	.044	.033	.048
.021	.021	.024	.029	.030	.022	.031
.012	.012	.014	.017	.017	.013	.018
.006	.006	.007	.008	.009	.007	.009
.003	.003	.003	.004	.004	.003	.004
.001	.001	.001	.001	.001	.001	.001

Specific Heat Functions.

potentials in chapter 6 is of negligible effect here; this is shown in fig. 7.2, where corresponding pairs of points have been plotted for the cases $V = 10.61$ cc , $V = 21.08$ cc. It is of more interest to consider the effect of varying f between wide limits, remembering it must be positive before the inflexion point, and negative beyond (the sign of ω^{0^2}); this is also illustrated in fig. 7.2, where dotted curves are drawn for $f = 1$ (the Debye curve), 0 , and -1 . It is clear that the approximations made, which lead to the choice of a particular average f_V at each volume, may effect the position of the corresponding $b_V(x)$ curve considerably; however, within reasonable limits, this is not important in the determination of $b_V(T)$ curves so long as the theory has to be fitted by means of the specific heat parameters Θ_{avge} ; if a theoretical prediction of Θ_D could be made accurately at each volume, then the absolute values of f_V would be of importance+. The possible variation of this sort in the $b_V(T)$ curves has been indicated in fig. 7.1. The values of the Θ_{avge} themselves are rather more sensitive to changes in f (given V); some extreme examples are quoted in table 7.2 below. It seems that the Θ_{avge}

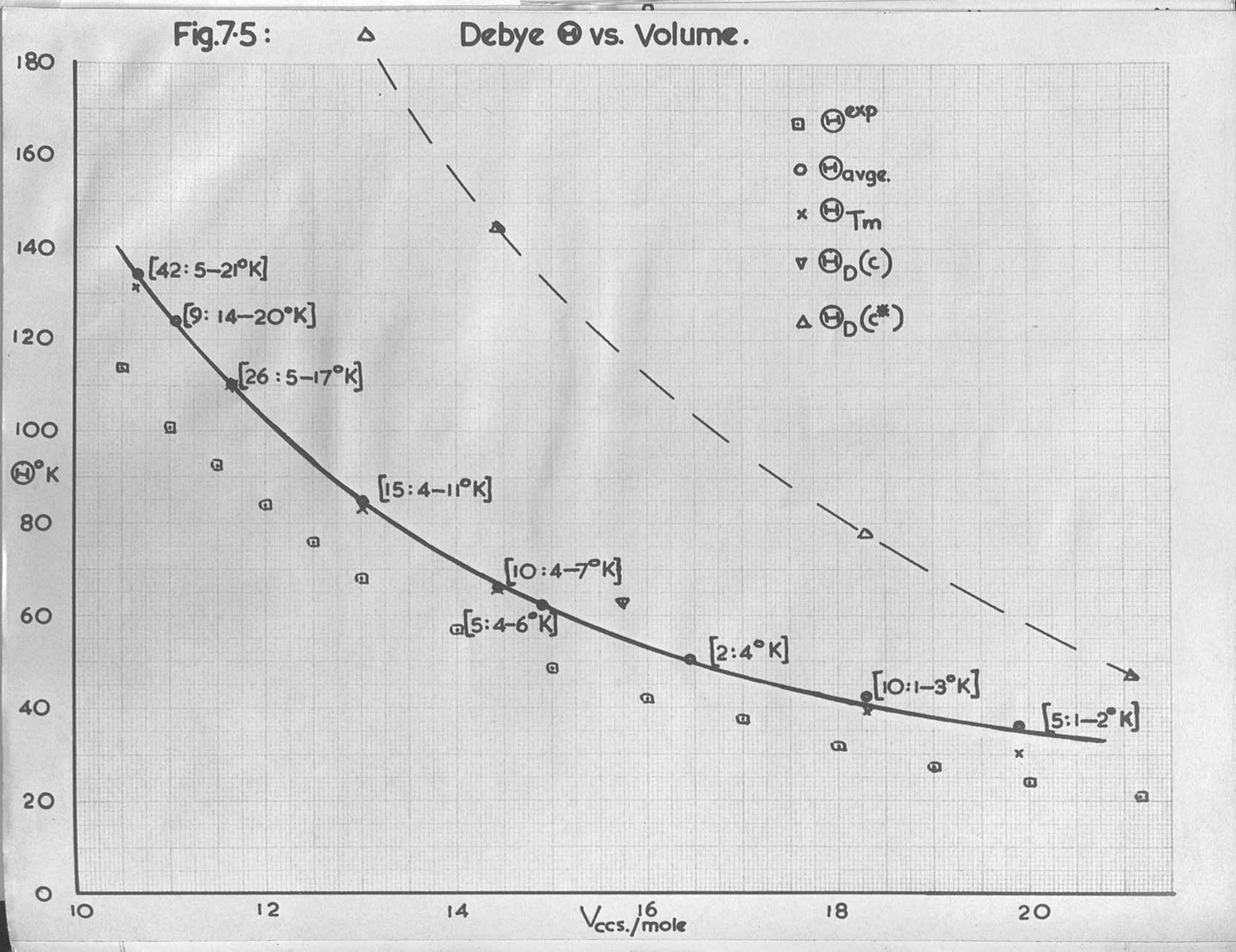
+ The values of the linear chain f are displaced from those of the lattice (e.g. $f \sim 0$ at 15.75 cc instead of at 14.39 cc) - the approximation is a n/n one in this respect.

calculated below using the linear chain f_V ought to be roughly correct. The assumption that f is constant along the spectrum, at constant volume, is evidently quite adequate, since agreement with experiment can be reached over a wide range of temperatures; it may, however, have a bearing on the increasing discrepancy near melting shown in fig. 7.1.

From the values of table 7.1 can be plotted very convenient curves showing the specific heat as a function of V for various values of x : these are of use in interpolating other volumes, the curves $b_V(x)$ being read off down the corresponding ordinate. They have been used for others of Dugdale's results than those in table 7.1, and for some of Keesom's results.

It remains to determine the Θ_T at each volume, by plotting the experimental specific heat $b_V^{exp}(T)$ on to the corresponding $b_V(x)$ curve, and taking the product of the abscissa (x) and T . This has been done for seven of Dugdale's volumes, and for two volumes used by Keesom ; some of the resulting curves have been plotted in fig. 7.3, in which Dugdale's Θ_T^{exp} are also shown. It is clear that the variation at each.

Fig.7·5 : △ Debye Θ vs. Volume.



volume is of no account compared to the differences between volumes. The average parameters (Θ_{avge}), as used in fig. 7.1, have then been calculated at these volumes: they are given in table 7.2, and plotted in fig. 7.5, where the number of observations associated with each is indicated. The Θ^{exp} chosen by Dugdale are also shown, and quoted in the table; for comparison, the Θ^{exp}_{avge} (which would be needed to fit Debye curves to fig. 7.1) are given as well. At large volumes (low temperatures) the calculated points diverge a little from the smooth curve drawn.

As mentioned earlier, the ratios of the Θ_{avge} at various volumes are not the same as those of the Θ^{exp} -- numerical values are given in table 7.2. The ratios of the empirical parameters needed to superpose the theoretical $b_v(x)$ curves are also shown: they must be multiplied by the ratios of the Θ_{avge} to be compared with those of Dugdale's Θ^{exp} -- the agreement is then, of course, very close, since the $b_v(T)$ and $b_v^{exp}(T)$ curves are very closely fitted. This empirical superposition property of the $b_v(x)$ implies that, at different values of b , the x for various volumes stand in constant ratio to one another, as can readily be shown numerically from the curves of fig. 7.2.

V ccs.	10.61	11.67	13.03	14.44	18.30
f_V	.309	.230	.163	.088	-.225
Θ_{avge} °K	134.92 (f=0:142.5) (f=1:115.5)	110.41 (f=1:93.3)	85.25	65.97 (f=0:66.5)	42.44 (f=0:42.1)
Θ_D °K (velocity c^*)	280.4	235.0	186.0	144.4	78.0
Θ_D °K (velocity c)	V = 15.75 cc: Θ_D = 63.0 °K				
Θ^{exp} °K	111.0	90.6	68.0	52.0	30.0
$\sim \left(\Theta_T^{exp}\right)_{melting}$ °K	112	92	71	54	39
$\sim \Theta^{exp}_{avge}$ °K	118	94	73	55	43
Ratios:-					
Θ_{avge}	2.046	1.676	1.291	1	0.644
$b_V(x)$ curves	1.042	1.022	1.017	1	0.958
product	2.130	1.710	1.312	1	0.617
$b_V(T)$ curves	2.113	1.714	1.310	1	0.601
Θ^{exp}	2.134	1.740	1.310	1	0.577

Table 7.2 : Debye Parameters.

As a theoretical relationship, it would mean that the volume dependence could be taken up by introducing a further reduced variable,

$$y = \frac{\vartheta}{x} ,$$

say; the single curve $b(x)$ should then really be written $b(y)$. There is no indication of such a property in the formula (7.1).

Finally, the $b_V(T)$ curves of fig. 7.1 must be calculated from Θ_{avge} and $b_V(x)$: values at these volumes are given in table 7.3. We may also construct curves showing the specific heat as a function of V for various values of T -- either by interpolation from the curves $b_x(V)$ or directly from the known $b_V(T)$ curves in fig. 7.1. They are of use in giving $b_V(T)$ at other volumes.

7c: Other Thermodynamical Properties.

The elastic determination of the Debye parameter Θ_D at any particular volume rests in the formulae given in chapter 4:

$$\Theta_D = \frac{h}{k}\sqrt[3]{\frac{3}{4\pi\Delta}}\,c , \qquad (7.4)$$

T °K	10.61 cc.	11.67 cc.	13.03 cc.	14.44 cc.	18.30 cc.
1					.023
1.5					.035
2					.092
2.5					.17
3					.31
3.5					T_m=3.1 °K
4	.018	.033	.078	.16	
4.5	.024	.047	.112	.25	
5	.033	.067	.153	.34	
5.5	.044	.090	.20	.44	
6	.061	.114	.26	.56	
6.5	.080	.15	.33	.72	
7	.097	.18	.41	.85	
8	.14	.27	.61	T_m=7.84 °K	
9	.20	.40	.84		
10	.28	.54	1.08		
11	.37	.70	1.35		
12	.49	.88	T_m=11.33 °K		
13	.60	1.06			
14	.75	1.27			
15	.88	1.47			
16	1.03	1.68			
17	1.17	1.90			
18	1.36	T_m = 17 °K			
19	1.52				
20	1.69				
22	2.03				
	T_m=23.39 °K				

Table 7.3 : Theoretical values of $b_v(T)$ (cals/mole).

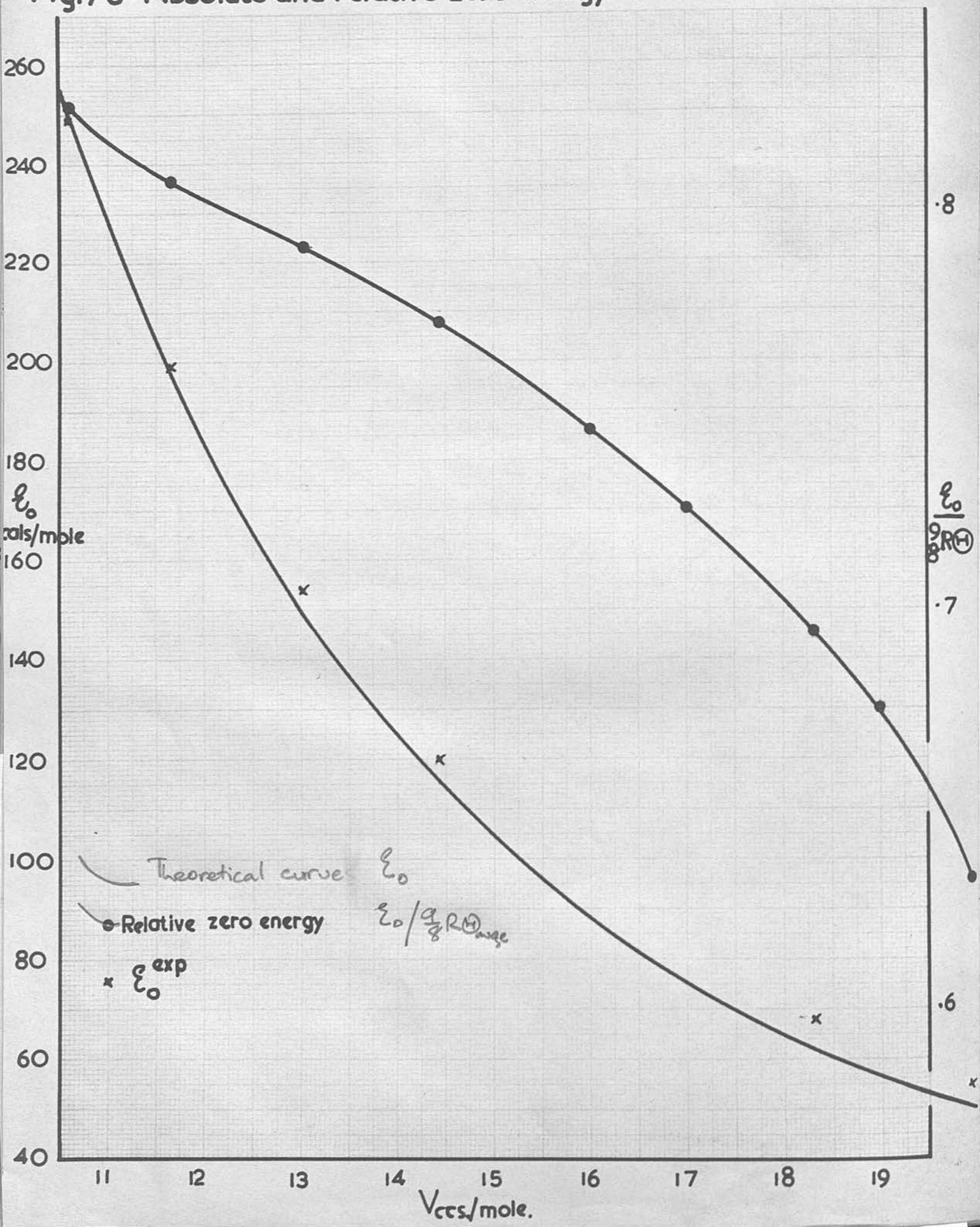
where $\Delta = \frac{V}{N} = \frac{1}{\sqrt{2}} a^3$, by (6.3), and c is the isotropic elastic velocity of the solid. As discussed in 4d, the strain-energy definition of c (4.17) can not be evaluated without an independent knowledge of the variation of the zero-energy, or of ω_D itself; there is no reason to use the experimental γ^{exp} (given in 7a) for this, as the corresponding Debye formula $\frac{9}{8} R \omega^{exp}$ quoted by Dugdale for ε_0 does not hold[+] in the non-linear theory; we should need to use γ_{awge} , got from the ω_{awge} as in fig. 7.4, in the hope that it corresponded with the variation of the unknown ω_D , together with the nonlinear formula from chapter 3:

$$\varepsilon_0 = \frac{f_{v+3}}{4} \cdot \frac{9}{8} R \omega_D(v) \; ; \qquad (7.5)$$

there would also remain some uncertainty in the other elastic factor of (4.17). The three-dimensional lattice spectrum is not known, so that the alternative definition of c is of no use; neither can any choice be made between the two approaches of Chapter 4.

+ This is in contrast to the rest of Dugdale's thermodynamical conclusions, based on a universal $\delta^{exp}(x)$ curve, with parameters ω^{exp} , which are quite self-consistent: only the formula for the zero-energy is inapplicable.

Fig. 7·6 : Absolute and relative zero energy vs. Molar volume.



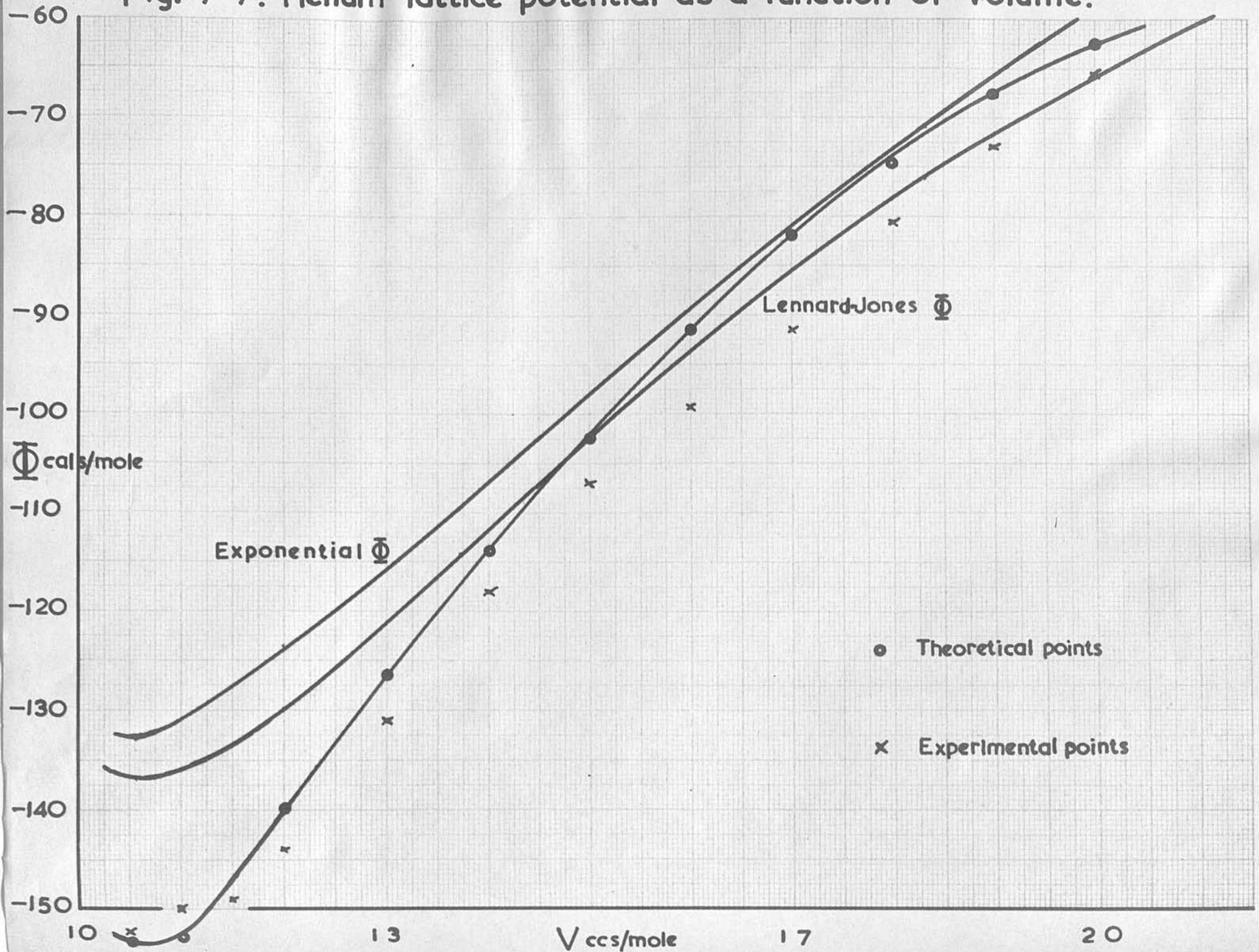
As a first approximation we can take c as the linear-chain elastic velocity c or c^*, of section 5e, given numerically in table 6.9. c^* is known for various volumes, and the corresponding Θ_D from (7.4) have been added to table 7.2; they are about twice too big as compared with the average specific heat parameters, though their dependence on volume is roughly the same. On the other hand the value of c at 15.75 cc which has been calculated lies fairly close to the Θ_{avge} curve, and again the volume dependence is expected to be similar. This may imply that the strain-energy definition of the Debye continuum is the appropriate one for thermodynamical purposes; on the other hand, the linear velocity approximation may be too crude to allow any useful conclusions to be drawn.

If we work out the zero energy from (7.5), using $\Theta_{avge}(v)$ from the graph of fig. 7.5, we get the values shown in table 7.4; the ratio $\epsilon_0 / \frac{9}{8} R\Theta$ has also been tabulated, as it is free of the uncertainties of the Θ -determination; the two curves are plotted in fig 7.6. Dugdale's

V ccs.	10.61	11.67	13.03	14.44	18.30	20
f_v	.309	.230	.163	.088	-.225	-.466
$\varepsilon_o / \frac{9}{8} R \Theta$	.827	.808	.791	.772	.694	.633
Θ_{avge} °K	135.0	109.5	84.5	67.0	40.5	35.0
ε_o cals/mole	249.2	197.1	148.7	115.2	62.3	49.2
ε_o^{exp} cals/mole	248	199	154	120	68	54

Table 7.4 : Zero energy of solid helium.

Fig. 7·7: Helium lattice potential as a function of volume.



calculated zero energy, based on the Debye formula $\frac{9}{8}R\Theta^{exp}$, is also shown -- it is not very different from the non-linear curve, and the discrepancy (some 10% of ε_0) is worst at large volumes, as is to be expected. For the Debye case, $\varepsilon_0/\frac{9}{8}R\Theta$ has the value 1.

The ε_0-curve has been subtracted from Dugdale's calculated curve for the internal energy at $T = 0^\circ K$, giving values for the lattice energy Φ. These are compared in table 7.5 with the calculations of chapter 6 (table 6.3), and shown graphically in fig. 7.7. There is good agreement except for the region of small molar volumes, near the minimum of the calculated Φ-curves, where the vibrational approach gives values some 10% too big: the present non-linear theory (with approximations) seems always to be weakest at small molar volumes. The Φ-calculations of chapter 6 themselves differ in this region from calculations based on the Slater-Kirkwood potential quoted by Dugdale (see London (1936)); this discrepancy has been indicated graphically in the paper of Yntema and Schneider referred to in chapter 6.

The Debye parameter Θ which enters into the Lindemann melting formula should strictly be the ω_D of chapter 4. This parameter arises when

V ccs.	ε_0 cals/mole	Internal Energy ($T=0^\circ K$) (Experimental)	$-\Phi$ cals/mole	(From Chapter 6) $-\Phi_{\text{Lenn-Jones}}$ cals/mole	$-\Phi_{\text{Experl.}}$
10.5	255.0	+101.5	153.5	136.5	132.5
11	228.5	+75.5	153.0	136.0	131.0
12	184.0	+44.5	139.5	130.0	124.0
13	150.0	+23.5	126.5	121.0	116.0
14	124.5	+10.5	114.0	111.5	107.0
15	104.5	+2.0	102.5	102.5	98.0
16	88.0	-3.5	91.5	94.0	89.5
17	75.0	-7.0	82.0	85.5	81.0
18	65.0	-9.8	74.8	78.0	73.0
19	56.5	-11.3	67.8	71.5	65.5
20	50.0	-12.0	62.5	66.0	57.5

Table 7.5 : Lattice energy of solid helium.

the lattice frequency spectrum is replaced by an isotropic Debye spectrum in forming the mean-square displacement $\overline{(x_\ell - x_\ell^{(0)})^2}$ of the atoms (see, for example, Peierls (1935), or Domb (1951)). This procedure is still permissible in the non-linear theory provided we understand the result to be the adapted harmonic approximation: we have, by (1.3), and the "non-linear" method of chapter 2, defined the "normal" coordinates q_k in the usual fashion, and they may then be written as the $e^{i\omega_k t}$ of the adapted harmonic oscillators to a first approximation. (the potential $V(q)$ is not entirely reduced to quadratic terms by the adaptation method). The "virtual" harmonic spectrum of the ω_k can thus be used, and leads to the result given by Domb,

$$\overline{(x_\ell - x_\ell^{(0)})^2} = \frac{q_k}{4M\omega_D}\left\{1 + \frac{2\pi^2}{3}\left(\frac{T}{\Theta_D}\right)^2 - 4e^{-\frac{\Theta_D}{T}}\left(\frac{T}{\Theta_D}\right)\left(1 + \frac{T}{\Theta_D}\right) + \ldots\right\}, \tag{7.6}$$

for small values of $\frac{T}{\Theta_D}$ (as here).

The ratio $\overline{(x_\ell - x_\ell^{(0)})^2}^{1/2}/a$ is given in table 7.6: the values calculated by Domb on the basis of Dugdale's Θ_{Tm}^{exp} are rather too large according to our non-linear theory.

V ccs.	$\frac{T_m}{\Theta_{T_m}}$	$\frac{1}{a}\overline{(x_2 - x_e^{MF})^2}^{\frac{1}{2}}$	
10.5	.207	.190	← Domb
10.61	.178 (.173)	.170	
11.67	.157 (.157)	.176	
13.03	.135 (.133)	.191	
14.0	.152	.228	← Domb
14.44	.120 (.120)	.205	
18.30	.079 (.073)	.238	
20.0	.088	.303	← Domb

Table 7.6: Vibrational Amplitude in Solid Helium.

In the table the parameter Θ_{T_m} is used -- the variation of Θ_T at constant volume is trivial except at very low temperatures where the Debye approximation is poor (see fig. 7.3); it is reasonable in the latter case to specify the Debye parameter near the melting temperature, in agreement

with the specific heat values; the ratio $\frac{T}{\Theta_{asymp}}$ has been indicated in brackets.

In Lindemann's harmonic theory, a constant value $\sim \cdot 1$ was predicted for $\overline{(x_l - x_l^{eq})^2}^{\frac{1}{2}}/a$; neither the theory nor the constant result are applicable to the non-linear helium case. But it is remarkable that the formula (7.0) is satisfied along the melting curve: the quantity

$$\frac{T_m^{\frac{1}{2}}}{\Theta V^{\frac{1}{3}}}$$

(which appears as the constant in Lindemann's high-temperature expression for $\overline{(x_l - x_l^{eq})^2}^{\frac{1}{2}}/a$: it does not arise in the low-temperature expression quoted above) remains constant; Dugdale's values based on $\Theta_{T_m}^{exp}$ (the remarks made above apply here also) are shown in table 7.7, together with

V ccs	T_m °K	$\frac{T_m^{\frac{1}{2}}}{V^{\frac{1}{3}}\Theta_{T_m}}$	$\frac{T_m^{\frac{1}{2}}}{V^{\frac{1}{3}}\Theta_{T_m}^{exp}}$
10.61	23.3	1.65×10^{-2}	1.96×10^{-2}
11.67	17.3	1.66	2.00
13.03	11.3	1.70	1.99
14.44	7.9	1.75	2.10
18.30	3.1	1.69	2.09

Table 7.7: The Lindemann Melting Relation for Helium.

those from the new theory which are a little more constant. The further comparison with other substances of Lindemann's full expression

$$K = \frac{m^{\frac{1}{2}} v^{\frac{1}{3}} \Theta}{T_m^{\frac{1}{2}}}$$

is made in table 7.8: the value of K got from the non-linear theory gives an even better agreement than is shown by Dugdale.

Substance	K
He ($\Theta^{exp}_{T_m}$)	99
He (Θ_{T_m})	118
Ne	140
A	162
Kr	163.5
Xe	164

Table 7.8 : Lindemann's Melting Constant for the Inert Gas Solids.

with the specific heat values; the ratio $\frac{T}{\Theta_{asymp}}$ has been indicated in brackets.

In Lindemann's harmonic theory, a constant value $\sim \cdot 1$ was predicted for $\overline{(x_2 - x_2^{eq})^2}^{\frac{1}{2}}/a$; neither the theory nor the constant result are applicable to the non-linear helium case. But it is remarkable that the formula (7.0) is satisfied along the melting curve: the quantity

$$\frac{T_m^{\frac{1}{2}}}{\Theta V^{\frac{1}{3}}}$$

(which appears as the constant in Lindemann's high-temperature expression for $\overline{(x_2 - x_2^{eq})^2}^{\frac{1}{2}}/a$: it does not arise in the low-temperature expression quoted above) remains constant; Dugdale's values based on $\Theta_{T_m}^{exp}$ (the remarks made above apply here also) are shown in table 7.7, together with

V ccs	T_m °K	$\frac{T_m^{\frac{1}{2}}}{V^{\frac{1}{3}}\Theta_{T_m}}$	$\frac{T_m^{\frac{1}{2}}}{V^{\frac{1}{3}}\Theta_{T_m}^{exp}}$
10.61	23.3	1.65×10^{-2}	1.96×10^{-2}
11.67	17.3	1.66	2.00
13.03	11.3	1.70	1.99
14.44	7.9	1.75	2.10
18.30	3.1	1.69	2.09

Table 7.7: The Lindemann Melting Relation for Helium.